**Kaunas University of Technology**

Faculty of Chemical Technology

# Synthesis of Polyvinyl Alcohol Gel Beads and Application for Wastewater Treatment

Master's Final Degree Project

**Judita Švaikauskaitė**

Project author

**lect. Inga Urniežaitė**

Supervisor

**Kaunas, 2021**

**Kaunas University of Technology**

Faculty of Chemical Technology

# Synthesis of Polyvinyl Alcohol Gel Beads and Application for Wastewater Treatment

Master's Final Degree Project

Environmental Engineering (6211EX003)

**Judita Švaikauskaitė**
Project author

**lect. Inga Urniežaitė**
Supervisor

**assoc. prof. Dalia Jankūnaitė**
Reviewer

**Kaunas, 2021**

**Kaunas University of Technology**

Faculty of Chemical Technology

Judita Švaikauskaitė

# Synthesis of Polyvinyl Alcohol Gel Beads and Application for Wastewater Treatment

Declaration of Academic Integrity

I confirm the following:

1. I have prepared the final degree project independently and honestly without any violations of the copyrights or other rights of others, following the provisions of the Law on Copyrights and Related Rights of the Republic of Lithuania, the Regulations on the Management and Transfer of Intellectual Property of Kaunas University of Technology (hereinafter – University) and the ethical requirements stipulated by the Code of Academic Ethics of the University;

2. All the data and research results provided in the final degree project are correct and obtained legally; none of the parts of this project are plagiarised from any printed or electronic sources; all the quotations and references provided in the text of the final degree project are indicated in the list of references;

3. I have not paid anyone any monetary funds for the final degree project or the parts thereof unless required by the law;

4. I understand that in the case of any discovery of the fact of dishonesty or violation of any rights of others, the academic penalties will be imposed on me under the procedure applied at the University; I will be expelled from the University and my final degree project can be submitted to the Office of the Ombudsperson for Academic Ethics and Procedures in the examination of a possible violation of academic ethics.

Judita Švaikauskaitė

*Confirmed electronically*

Judita Švaikauskaitė. Synthesis of Polyvinyl Alcohol and Application for Wastewater Treatment. Master's Final Degree Project/supervisor lect. Inga Urniežaitė; Faculty of Chemical Technology, Kaunas University of Technology.

Study field and area (study field group): Environmental Engineering (E03), Engineering Sciences.

Keywords: polyvinyl alcohol, gel beads, sorption, wastewater treatment.

Kaunas, 2021. 64 p.

## Summary

Water is an integral part of our daily lives. Therefore, clean water must be available to everyone. Pollutants that enter the environment pose a significant threat to human health and the ecosystem as a whole. For this reason, water quality is a growing concern globally, and measures are being taken to apply water treatment not only to traditional but also to advanced methods.

Advanced oxidation, biological treatment, membrane filtration, and other technologies are commonly used to remove contaminants from water. These days, much attention is paid to advanced water treatment technologies that help to improve water quality faster, more efficiently, and without requiring significant infrastructure changes. In recent decades, there has been an increasing focus on hydrogels, and they are expected to be suitable for biological water treatment. Hydrogel gel beads have macro-pores that are of a suitable size for immobilizing microorganisms.

One of the alternative polymers suitable for the production of gel beads is polyvinyl alcohol. Polyvinyl alcohol gel beads have a three-dimensional gel network bonded by chemical or physical bonds. Polyvinyl alcohol gel beads also have good mechanical resistance and are therefore suitable for long-term use.

The production of polyvinyl alcohol gel beads consists of several main steps: preparing a solution of polyvinyl alcohol with additives and dropping it into a crosslinking solution. Sorption studies of the prepared gel beads are performed using UV-VIS spectrophotometric analysis. Different types of gel beads are placed in solutions of different types and concentrations of micro-contaminants, and their sorption is monitored. Gel beads of polyvinyl alcohol with chitosan and polyvinyl alcohol with boric acid are used in the study. Three micro-contaminants were selected for the sorption properties study: sulfamethoxazole, tetracycline, and methylene blue. Sorption studies are performed for 300 minutes, and light absorption is monitored. Based on the obtained sorption results, the sorption capacity of the gel beads and reaction rates are calculated.

The polyvinyl alcohol gel beads produced are also tested in a biological system. Five reactors filled with mixtures of gel beads and activated sludge are used for this purpose. The study is conducted for seven days, and the changes in the parameters of synthetic wastewater are monitored. In addition, nitrates, phosphates, ammonium, total nitrogen, phosphorus, and organic carbon in the reactors are monitored during biological treatment.

Judita Švaikauskaitė. Polivinilo alkoholio granulių sintezė ir jų panaudojimas nuotekų valymui. Magistro baigiamasis projektas/vadovė lekt. Inga Urniežaitė; Kauno technologijos universitetas, Cheminės technologijos fakultetas.

Studijų kryptis ir sritis (studijų krypčių grupė): Aplinkos inžinerija (E03), Inžinerijos mokslai.

Reikšminiai žodžiai: polivinilo alkoholis, granulės, sorbcija, nuotekų valymas.

Kaunas, 2021. 64 p.

## Santrauka

Vanduo yra neatsiejama mūsų kasdieninio gyvenimo dalis. Todėl labai svarbu, kad švarus vanduo būtų prieinamas kiekvienam žmogui. Teršalai, kurie patenka į aplinką, kelia didelį pavojų ne tik žmogaus sveikatai, bet ir visai ekosistemai. Dėl šios priežasties, pasaulyje vis didesnį susirūpinimą kelia vandens kokybė ir imamasi priemonių vandens valymui taikyti ne tik tradicinius, bet ir pažangiuosius metodus.

Pažangioji oksidacija, biologinis valymas, membraninis filtravimas ir kitos technologijos yra dažniausiai naudojamos norint pašalinti teršalus iš vandens. Šiomis dienomis didelis dėmesys skiriamas pažangiosioms vandens valymo technologijoms, kurios padeda greičiau, efektyviau ir nereikalaujant didelių infrastruktūros pokyčių, pagerinti vandens kokybę. Pastaraisiais dešimtmečiais vis daugiau dėmesio skiriama hidrogeliams ir tikimasi, kad jie bus tinkami biologinio vandens valymo metu. Hidrogelio granulės pasižymi makro-poromis, kurios yra tinkamo dydžio mikroorganizmams imobilizuoti.

Vienas iš alternatyvių polimerų, tinkamų granulių gamybai yra polivinilo alkoholis. Polivinilo alkoholio granulės pasižymi trimačiu gelio tinklu, sujungti cheminiais ar fizikiniais ryšiais. Taip pat polivinilo alkoholio granulės pasižymi geru mechaniniu atsparumu, todėl yra tinkamos ilgalaikiam naudojimui.

Polivinilo alkoholio granulių gamybą sudaro keli pagrindiniai etapai: polivinilo alkoholio tirpalo su priedais paruošimas ir jo lašinimas į tinklinimo tirpalą. Paruoštų granulių sorbcijos tyrimai vyksta naudojant UV-VIS spektrofotometrijos analizę. Skirtingų rūšių granulės yra patalpinamos į skirtingų rūšių ir koncentracijų mikro-teršalų tirpalus ir stebima jų sorbcija. Tyrime naudojamos polivinilo alkoholio su chitozanu ir polivinilo alkoholio su boro rūgštimi granulės. Sorbcinių savybių tyrimui pasirinkti trys mikro-teršalai: sulfametoksazolis, tetraciklinas ir metileno mėlis. Sorbcijos tyrimai vykdomi 300 minučių ir stebima šviesos sugertis. Pagal gautus sorbcijos, rezultatus apskaičiuojama granulių sorbcinė geba ir reakcijų greičiai.

Pagamintos polivinilo alkoholio granulės taip pat išbandomos ir biologinėje sistemoje. Tam naudojami penki reaktoriai užpildyti granulių ir aktyviojo dumblo mišiniais. Tyrimas vykdomas septynias dienas ir stebima kaip keitėsi sintetinių nuotekų parametrai. Stebimi nitratų, fosfatų, amonio, bendro azoto, fosforo ir organinės anglies kiekiai reaktoriuose, vykstant biologiniam valymui.

## Table of contents

## List of figures

# List of tables

## List of abbreviations

**Abbreviations:**

AS – sctive sludge;

BA – boric acid;

CS – chitosan;

DI – dionized water;

HG – hydrogel;

ID – inner diameter;

PBS – phosphate buffered saline;

PVA – polyvinyl alcohol;

PVA/BA – polyvinyl alcohol gel beads with boric acid;

PVA/CS – polyvinyl alcohol gel beads with chitosan;

$SiO_2$ – silica gel;

TN – total nitrogen;

TOC – total organic carbon;

TP – total phosphorus;

UV – ultraviolet radiation;

WWTP – wastewater treatment plants.

# Introduction

The world's water resources are being polluted due to the discharge of many pollutants such as heavy metals, surfactants, pharmaceuticals, pesticides, etc. As a result, this becomes an issue requiring urgent attention [1]. Hydrogels are three-dimensional hydrophilic, insoluble cross-linked polymer networks with characteristically very high swelling capacity. The high-water content and elastic characteristics of hydrogels allow them to absorb a large volume of aqueous solution inside its three-dimensional reticulates networks better than any other class of synthetic biomaterials [2]. Due to the effective sorption of the broad class of organic and inorganic aqueous pollutants, hydrogels have been considered for a wide range of applications, particularly in wastewater treatment [3].

The base materials are cross-linked through different chemical or physical routes that impart a three-dimensional gel network [2]. The synthesis mechanism of the polyvinyl alcohol with boric acid gel beads consists of two steps: (1) unlocking of the intrinsic cross-linking hydrogen bonds in the PVA chains by sodium hydroxide (2) forming of cross-link networks when the alkali PVA is dropped in the boric acid solution [4]. During polyvinyl alcohol with chitozan gel beads synthesis, chitozan is attracted to hydroxyl groups in PVA molecules to achieve hybrid cross-linking [4]. Chitosan is a natural chelating agent which rich in active amino groups, protonic enough to carry positive charges [5]. Due to these properties, chitosan is a suitable additive for the production of gel beads. The sorption capacity of PVA/CS and PVA/BA gel beads was investigated using micro-pollutants such as Sulfamethoxazole, Tetracycline, and Methylene blue. UV-VIS spectroscopy was used to monitor the sorption process.

PVA/CS and PVA/BA gel beads with diameters of 2-4 mm were successfully synthesized using a cross-linking method. PVA/BA gel beads had better mechanical strength. The study confirmed the efficiency of the PVA/CS and PVA/BA gel beads as the sorption agents. The removal efficiency of Tetracycline using PVA/CS gel beads is 74.0%. Similar efficiency was found for adsorption using PVA/BA gel beads, which was about 65.8%. The highest efficiency was found in removing Methylene blue, the concentration of which in the solution was reduced by 78.2% using PVA/CS gel beads and 97.9% using PVA/BA gel beads.

This research aims to clarify the synthesis mechanism of polyvinyl alcohol/chitosan (PVA/CS) and polyvinyl alcohol/boric acid (PVA/BA) beads and evaluate their feasibility in wastewater treatment.

Objectives:

- Conduct a literature review addressing issues related to the mechanism of adsorption and desorption, the current knowledge on different carriers, and synthesis of macroporous beads.
- Develop the synthesis methods for polyvinyl alcohol hydrogel beads.
- Evaluate the adsorption capacity of different polyvinyl alcohol hydrogel beads.
- Investigate and compare the pollutants removal behavior of microporous gel beads for biological wastewater treatment.

# 1. Literature review

## 1.1. Biological wastewater treatment using carrier materials

A persuading wastewater treatment office is a fundamental reason for guaranteeing a perfect climate. One of the primary cycle steps in a wastewater treatment plant includes organics by miniature life forms [6]. Similarly, as any living animal, these miniature living beings need oxygen to endure. This oxygen is most usually embedded via air infusion straightforwardly into the wastewater. The interaction can be improved by adding solid surfaces to the water compartment. These surfaces give the miniature living beings a spot to grow up, and their home time is longer than the one of the water. For a smooth cycle, it is fundamental to pick the ideal transporters. Regardless of whether the cycle requires organic conveying media for streaming channels, arbitrary or suspended beds, the entirety of the accompanying prerequisites should be satisfied [7]:

- High specific surface area;
- Good permeability of the wastewater;
- Optimum size and configuration in respect of price and durability;
- Suitable to be cleaned by water flowing through;
- Non-toxic material to ensure the life of the micro-organisms.

For the most part, biofilm-based wastewater treatment frameworks enjoy a few upper hands over ordinary initiated slop measures, like their high dynamic biomass focus, low space necessities, decreased pressure-driven maintenance time, more steady execution, and low slime creation. Significantly, microbial networks in biofilms will, in general, be more assorted than those in enacted slime frameworks, permitting debasing a broad scope of natural toxins, for example, drugs and individual consideration items [6].

### 1.1.1. Carriers

Because of the idea of materials, transporters in natural wastewater treatment can be ordered into three gatherings: inorganic material-based microbial transporters, natural material-based transporters, and engineered polymeric sorbents [6].

#### 1.1.1.1. Inorganic materials-based microbial carriers

Inorganic materials like zeolite, volcanic stone, earthenware production, and enacted carbon are frequently utilized as biofilm transporters in natural wastewater treatment measures [8]. Another examination utilized earthenware production as transporters in moving bed biofilm reactor to treat oilfield wastewater [10]. These transporters likewise have stable compound properties. What is more, inorganic materials-based transporters will, in general, have an enormous explicit surface region [11]. For instance, the particular surface spaces of ceramsite and zeolites frequently fluctuate from 500 to 1200 $m^2/m^3$ and 300 to 1000 $m^2/m^3$, individually. Additionally, inorganic materials-based transporters' harsh surface and overall pore structure permit shielding microorganisms from stun loads while likewise giving a phenomenal climate to biofilm connection.

Zeolite was demonstrated to have preferred adsorptive expulsion proficiency over other inorganic transporters (i.e., ceramics and actuated carbon) in treating nitrogen-containing wastewater. For instance, tracked down that the expulsion productivity of nitrogen by zeolite-based transporters could be 89.6%, while it was just 65.1 and 35.6% by ceramsite and light-permeable media, separately.

Higher evacuation of ammonium-nitrogen saw in zeolite-based transporters contrasted with other inorganic materials-based transporters (i.e., ceramsite and light-permeable media) could be ascribed to the particle trade property zeolite, which permits eliminating ammonium-nitrogen through adsorption instrument [13].

Inorganic materials-based transporters, for example, zeolite and enacted carbon, show remarkable sorption properties. Like this, these transporters are frequently used to eliminate weighty metals in wastewater treatment. However, the evacuation efficiencies of hefty metals by these transporters appear to be moderately low [8].

Aside from the benefits above, inorganic materials-based biofilm transporters have a few inconveniences identified with moderate biofilm development, helpless penetrability, enormous stream opposition, and simple obstructing [12].

#### 1.1.1.2. Organic material-based carriers

Organic materials-based carriers are widely used as microbial carriers in wastewater treatment. For example, used polyvinyl alcohol (PVA)-gel beads as a biomass carrier in UASB reactor to enhance the removal of organic nutrients in wastewater [14].

Natural materials-based transporters, for example, alginate and bamboo fibber, have significant biocompatibility and hydrophilicity. However, in the interim, these materials, like bamboo, are moderately modest for functional application.

By and large, the surface design of common natural materials-based transporters works with adherence to microorganisms, particularly this sort of biofilm transporter is not poisonous to cells and simple to handles after use, and does not cause ecological contamination [15].

As it may, ordinary natural materials-based biofilm transporters frequently display low mechanical strength, helpless mass exchange execution, and fast corruption by microorganisms. Therefore, the reuse of these biofilm transporters is generally restricted. Likewise, the unsteady arrival of dissolvable carbon hotspots for denitrification during wastewater treatment is viewed as another disadvantage of this sort of transporter [6].

#### 1.1.1.3. Synthetic polymeric sorbents

In recent decades, various endeavors have been made to foster latent natural materials for biofilm transporters, e.g., polyvinyl alcohol, polystyrene, polyester, and different materials required to conquer responsive, natural materials constraints as biofilm carriers.

Typically, inert organic materials-based biofilm carriers (e.g., polypropylene, polyethylene, polystyrene, and polyurethane) are known to have low density, stability, resistance to biodegradation and aging, and substantial mechanical strength, but their large specific surface area is still limited (460–900 $m^2/m^3$) [16].

Hydrogels (HG) are being used in diverse sectors like biomedical engineering, food technology, agricultural engineering, and water resource engineering. Hydrogels offer large scale of flexibility in rapid swelling kinetics, modifiable surface characteristics such as charge, functionality, fast diffusion process, large area, controllable pore structure, permeability catalysis, fast kinetics, thermo-stability, interesting acid/base properties, and hydrophilicity. In water treatment applications, HGs are exceptionally successful in controlling a broad class of natural and inorganic fluid pollutants, including including metal ions, harmful dyes, and pestilential pharmaceutical wastes [7].

An energizing and reasonable utilization of HGs in the use of HG for entanglement and immobilization of enacted muck (AS). AS which contains likely microorganisms for the expulsion of biodegradable segments from the wastewater. The use of live biomass (microorganisms, green growth) in natural wastewater treatment presents numerous limits due to delicately towards various boundaries, for example, high fixation heap of pollutant, pH, and temperature [16].

### 1.1.2. Removal mechanism of pollutants and factors affecting removal in biological reactors filled with carriers

Total comprehension of the adsorption cycle and expulsion component of various pollutants on particular hydrogels is fundamental for upgrading and changing the HG properties. Due to the complex composition of HGs, the characterization of the sorption process of metal ions is a complex phenomenon and needs through understanding of process parameters [7].

The performance efficiency along with selectivity primarily depends on the chemical network within HGs. The different sorption mechanism of contaminants by HGs has been illustrated in Figure 1 [7].

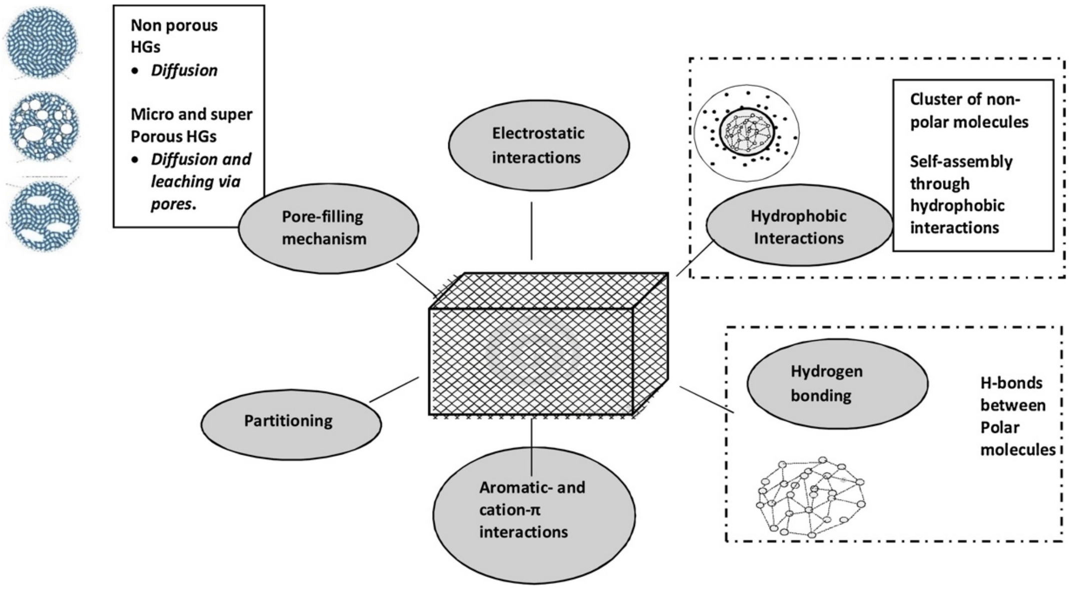


**Figure 1.** Sorption mechanism of different contaminants by HGs [7]

## 1.2. Fundamentals of adsorption and desorption

Adsorption – desorption reactions are important processes that affect the transport of contaminants in the environment.

### 1.2.1. Surfactants

Surfactants are substance intensifies that are utilized for various mechanical and homegrown applications. Surfactants are ordered into four fundamental classes dependent on the charge on the head bunch. These are; anionic, cationic, non-ionic, and amphoteric. The synopsis of the principle surfactant classes is in Figure 2. The head gathering of surfactants characterizes their personality and properties. Surfactants are utilized in numerous applications for various purposes, for example, frothing, wetting, emulsion adjustment, mineral detachments, detergency, drug details, and different purposes. The high convergences of surfactants found in wastewaters result from their far and wide applications in current life [6].

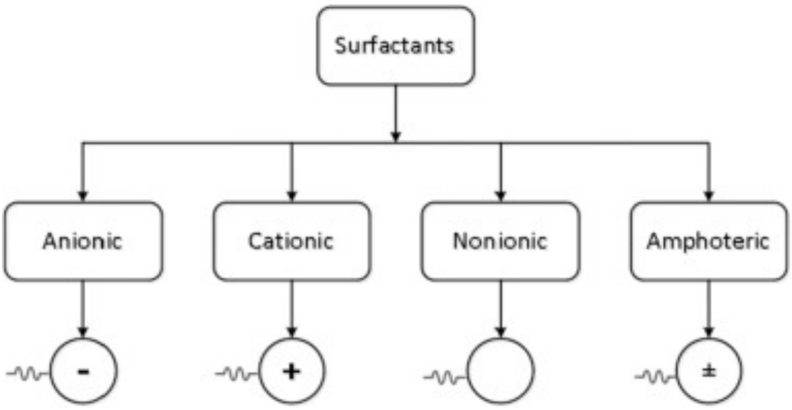


**Figure 2.** Types of surfactants [6]

Adsorption

Adsorption has emerged as an essential process for various industrial applications, such as natural gas storage, pollution control, catalyst supports, especially gas separation and purification, because of its less energy intensiveness, highly flexible cycling, and availability of various adsorbents [17]. Also, adsorption has been viewed as one standard strategy for deciding the surface region and permeable size dissemination of solid materials. Accordingly, a basic comprehension of the adsorption component requests to plan and enhance the modern adsorption measure and the portrayal of the design of porous solids.

Adsorption is a method for separating substances at the interface of two phases such as liquid-liquid, gas-liquid, gas-solid, and liquid-solid. Adsorption may be classified into two classes: (1) physisorption and chemisorption, depending on the adsorbate–adsorbent interactions. The former is characterized as reversible, while the latter is irreversible due to chemical bonding [18].

The reusing or recovery of the adsorbent materials is the real benefit of the adsorption procedure, making it affordable. The reusing of the adsorbent relies upon the desorption or recovery proficiency of the adsorbent. The adsorption of surfactants relies upon the properties of adsorbent, adsorbate, and arrangement — the qualities of an adsorbent incorporate surface region, pore size, pore-volume, and surface charge. The adsorbate properties incorporate usefulness, math, hydrophobicity, atomic weight, dipole second, extremity and size, and dissolvability in a fluid arrangement. The properties of the arrangement incorporate pH, pressure, temperature, ionic strength, adsorbate focus, and the presence of foundation and serious solutes. The properties of adsorbate, adsorbent, and arrangement assume indispensable parts in the adsorption of surfactants [18].

A large number of adsorbents have been developed for the removal of surfactants from wastewater. The adsorbents can be categorized into organic and inorganic. Selected adsorbents and their adsorption performance are described below about their characteristics.

### 1.2.2. Organic adsorbents

Activated carbon could be the most suitable material for the adsorption of pollutants from wastewater. It possesses a high surface area in the range of 600–2000 $m^2/g$ and a well-defined microporous structure. The synthesis of activated carbons using economical raw materials and efficient regeneration can improve activated carbon in the removal of surfactants [18].

The nanomaterials perform very well in the adsorption of surfactants with higher adsorption limits and evacuation efficiencies. In any case, the considerable scope utilization of nanomaterials is restricted because of troublesome partition, spillage into contact waters, and unfriendly consequences for biological systems and human wellbeing.

Chitosan is a renewable, economical, and widely available biomaterial. It is a biodegradable, biocompatible, and decidedly charged nontoxic biopolymer. It is created from chitin by deacetylation. Chitin comprises N-acetyl glucosamine, and it is the most bountiful normal polysaccharide after cellulose [19]. Chitin is gotten from the exoskeletons of shellfish, bug fingernail skin, and contagious biomass. Be that as it may, the adsorption limit of unmodified chitosan is low contrasted with altered chitosan adsorbents for the adsorption of anionic surfactants, by and large from writing discoveries.

### 1.2.3. Inorganic adsorbents

Zeolites are suitable adsorbents for the removal of pollutants from wastewater. The pore size and hydrophobicity of zeolites assumed fundamental parts in the adsorption/oxidation of surfactant. Different examples of inorganic adsorbents could be clays, alumina, fly ash, cellulose, carbon black [20].

Inorganic adsorbents have high selectivity, large adsorption capacity, and a high recovery rate [20].

### 1.2.4. Properties of adsorbents for removal of different types of surfactants

An assortment of adsorbents has been produced for the removal of ionic, non-ionic, and amphoteric surfactants. The essential properties of adsorbents for eliminating surfactants are porosity, surface region, pore size, and pore volume. The higher the porosity of adsorbents higher is the adsorption of surfactants. The higher porosity delivers a higher surface region which builds the adsorption of surfactants.

The pore size of the adsorbents decides their adsorption execution. Adsorbents can be characterized as macroporous, mesoporous, and microporous, depending on pore size or pore distance. Macroporous, mesoporous and microporous materials have pore sizes of >50 µm, > 2 µm < 50 µm, and > 2 µm. Surfactants are enormous atoms that cannot be caught utilizing microporous materials. Macro and mesoporous materials are more suitable for larger molecules like surfactants [20]. Macro and mesopores will enhance the adsorption of surfactants of the higher pore volume.

### 1.2.5. Characteristic of desorption

Desorption is the converse interaction, i.e., the disposal of the adsorbed substances from the surface. Desorption is the arrival of one substance from another, either from the surface or through the surface. Recovering adsorbents is vital for reusing the adsorbents and recuperating the adsorbate separated from the arrangement. Conditions preferring the desorption of contaminations from the adsorbent give an understanding of the adsorption component. Proficient adsorption and desorption are the critical attributes of good adsorbent material. Furthermore, the recovery of the adsorbent assists with improving the financial feasibility of the cycle [6].

Desorption is necessary, and it is conducted after adsorption. However, the optimization of desorption conditions is typically a more challenging and time-consuming process [21]. The desorption process involves the optimization of:

- desorption solvent;
- solvent volume;
- desorption time;
- evaluation of carryover.

*Desorption* is a different process from adsorption, which happens as a last synergist step in heterogeneous-catalyzed responses. It eliminates surface-adsorbed species and prepares the surface for additional adsorption by new reactant particles [22].

At low temperatures, adsorbed species, for the most part, are held on a superficial level. Notwithstanding, when the temperature expands, the adsorbed particle may disintegrate and go through the surface response between the particles or nuclear species; further, it will desorb from the surface and get back to the vaporous stage [2].

## 1.3. Fundamentals of biodegradation and biosorption

### 1.3.1. Biodegradation

Biodegradation is the degradation of the materials into ecologically adequate items like water, carbon dioxide, and biomass by the activity of ordinarily accessible microorganisms under ordinary natural conditions.

In the natural setting, by and large, microorganisms are the primary specialists of biodegradation. Although extensive degradation of some xenobiotic chemicals can occur in mammals (usually in the liver), they are not particularly important in the degradation of environmental pollutants. The heterotrophic bacteria are often considered of prime importance; however, the role of fungi is increasingly recognized. Algae and cyanobacteria can catalyze some biodegradative processes but are probably of only limited importance. Varying degrees of biodegradation can occur according to how much the compound has been modified [23].

*Biodegradation* is a natural process by which organic chemicals in the environment are converted to simpler compounds. Biodegradation can happen inside the biosphere as microorganisms assume a focal part in the biodegradation interaction. There are four biodegradation conditions for polymers and plastic items: soil, oceanic, landfill, and fertilizer. Every climate contains various microorganisms and has various conditions for corruption. For example, in soil, fungi are primarily responsible for the degradation of organic matter, including polymers [24].

The aquatic environment is overwhelmed by two sorts of microscopic organisms, by all accounts and in the silt, with a bacterial fixation in water diminishing with expanding profundity. Microorganisms biodegrade natural materials by utilizing their enzymatic, mechanical assembly; in any case, microorganisms have not yet had the opportunity to adjust and integrate polymer-explicit proteins equipped for debasing and devouring manufactured polymers of ongoing beginning. Thus, the measure of non-degradable plastic waste can be essentially diminished by the appropriate advancement of biodegradable polymers and composites for transient items [23].

Biodegradation can occur by two different mechanisms: namely hydro-biodegradation (hydrolysis followed by oxidation) and oxo-biodegradation.

### 1.3.2. Biosorption

Sorption-based and ion-exchange processes are well-known efficient methods for recovering trace amounts of precious metals from aqueous systems.

*Biosorption* is a physic-chemical and metabolically independent process based on various mechanisms, including absorption, adsorption, ion exchange, surface complexation, and precipitation. Biosorption measures are crucial in the climate and regular biotreatment measures. As a part of biotechnology, biosorption has been focused on the evacuation or recuperation of natural and inorganic substances from the arrangement by organic material, which can incorporate living or dead microorganisms and their segments, ocean growth, plant materials, modern and agrarian squanders, and normal buildups [24].

### 1.3.3. Bio-sorbents

Bacteria, algae, fungi, the skin of animals and fruits, plant residues, active sludge, and biopolymers are different bio-sorbent. Researchers believe that adsorbents extracted from biological sources are classified as bio-sorbents. Commercial bio-sorbent should meet the following criteria [25]:

- High biosorption capacity and suitable kinetics;
- Good size, shape, and physical properties;
- The separation of bio-sorbents from solutions should be cheap, fast, and high-performing;
- Strong mechanical strength, thermal stability, and good chemical resistance;
- Availability of bio-sorbents and cost-effective preparation methods;
- Being regeneratable and reusable.

Because of the ability of any cell for biosorption, there are various ways to deal with the group the bio-sorbents. In an overall characterization, biomasses can be isolated into two gatherings: dead and alive. The dead biomasses can be utilized in long-haul biosorption-desorption cycles. In any case, most dead biomasses have a generally low mechanical strength and a gentle structure with fantastic molecule size. Like this, this marvel prompts impressive loss of bio-sorbent during the recuperation and troublesome detachment of spent bio-sorbent from treated arrangement [26].

Bio-sorbent preparation processes have several cost-effective steps [24]:

1. providing raw bio-sorbent;
2. pre-treatment of bio-sorbents (washing, sizing, purification, and treatment of bio-sorbents for modification);
3. analyzing the bio-sorbent produced on a bench scale.

### 1.3.4. Biosorption effective factors

Valuable elements on biosorption incorporate temperature, pH, bio-sorbent portion, response time, and practical gatherings. Moreover, the underlying convergence of dissolvable matter, blending, and bio-sorbent size likewise add to bioavailability. Figure 3 shows the schematic of the biosorption interaction [24].

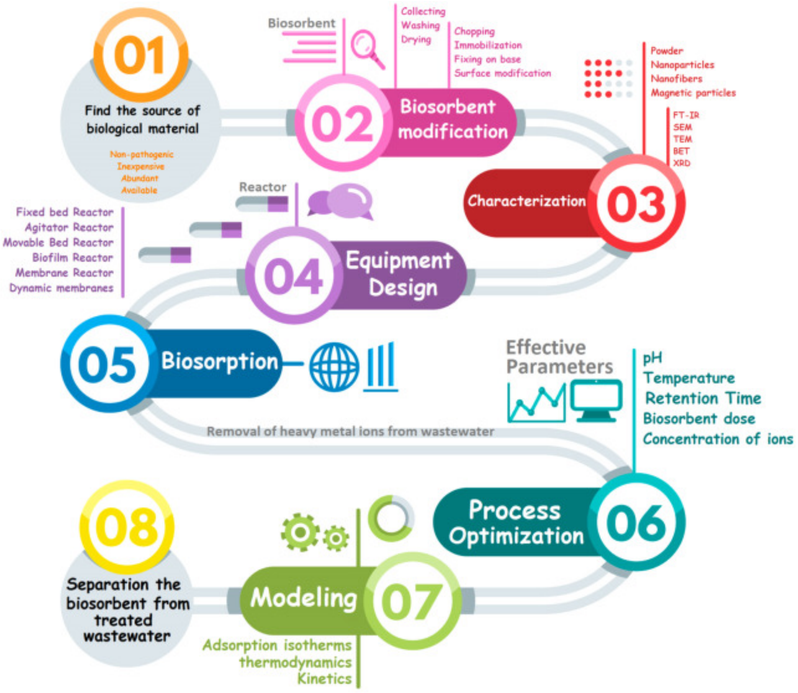


**Figure 3.** Schematics of the biosorption process [24]

### 1.3.5. Biosorption mechanism

Understanding the instrument by which microorganisms retain metals is troublesome and complex because of the intricacy of the cell mass of biomaterials and the mind-boggling science of the metal complex, and the failure to decide the edifices present arrangement correctly. By and large, in the biosorption cycle, the association systems of the biosorption are hazy.

The biosorption by microorganisms is identified with the ligands present in their polymer divider particles. Biosorption includes a blend of a few components like electrostatic fascination, complexation, particle trade, covalent powers, van der Waals powers, surface adsorption, and microstructure sequestration [24]. The interaction of adsorption of metal particles by bio-sorbent can be depicted in two stages.

The initial step is developing the solute mass containing the particle and the particle arriving at the adsorbent surface, which is a generally quick measure and can be sped up by explicit strategies, for instance, by mixing the arrangement [26].

The subsequent advance moves the broken-down segment from the adsorbent surface to the inside dynamic destinations and connects the disintegrated and dynamic locales, which is a generally lethargic cycle. Cell divider polymers incorporate numerous substance gatherings like hydroxyl, carbonyl, carboxyl, sulfhydryl, thioether, sulfonate, amine, imine, amide, imidazole, phosphonate, and phosphodiester. These substance gatherings of the biopolymers are fortified together and furnish ligand particles to shape buildings with metal particles [26].

The biosorption mechanism can be defined as follows [14]:

1. Cell surface penetration;

2. Adsorption;
3. Make connections with surface groups;
4. Transfer metal to active or inactive cell;
5. Organic-metal bonding (Metal stops the biomass metabolic process).

### 1.4. Synthesis and characterization of macroporous beads for biological wastewater treatment

Hydrogels are three-dimensional polymeric bead networks that swell in contact with water but maintaining their structural integrity. There is growing interest in hydrogels because of their excellent biocompatibility, easy preparation, and versatile applications.

#### 1.4.1. Hydrogel characterization

Nowadays, polymers are employed in a multidisciplinary field of research, and hydrogels are being used in diverse sectors like biomedical engineering, food technology, agricultural engineering, and water resource engineering. Hydrogels offer a large scale of flexibility in rapid swelling kinetics, modifiable surface characteristics such as charge, functionality, fast diffusion process, large area, controllable pore structure, permeability catalysis, fast kinetics, thermo-stability, interesting acid/base properties, and hydrophilicity. In water treatment applications, HGs are very effective for the containment of a broad class of organic and inorganic aqueous pollutants, including metal ions, harmful dyes, and pestilential pharmaceutical wastes [7].

**Figure 4.** Acrylic based hydrogels [30]

The usage of live biomass (bacteria, algae) in biological wastewater treatment presents many limitations due to sensitively towards different parameters such as high concentration load of contaminant, pH, and temperature.

PVA gel polymers were widely used in biocatalyst because of their low cost, non-toxic, porous, high mechanical strength, and elastic nature. Wang and co-workers prepared the shape stable PVA-sodium alginate HGs with immobilized sludge. These HGs maintained excellent stabled structure and bio-catalytic activity under repeated dry-rewet cycles along with sufficient bioactivity for COD degradation. In addition, the porous HG was found to increase the substrate and oxygen diffusion rate that fastened the biodegradation rate. Thus, HGs, as an immobilization carrier, aids in enhancing the biodegradation rate, increase process control, improves bioactivity, and provides stable and milder conditions to biocatalysts.

Due to these physicochemical characteristics, there is an increasing interest in tuning and designing novel HGs for wastewater remediation and monitoring usage. Different modification methodologies and properties of HGs for wastewater treatment can be seen in Figure 5 [7].

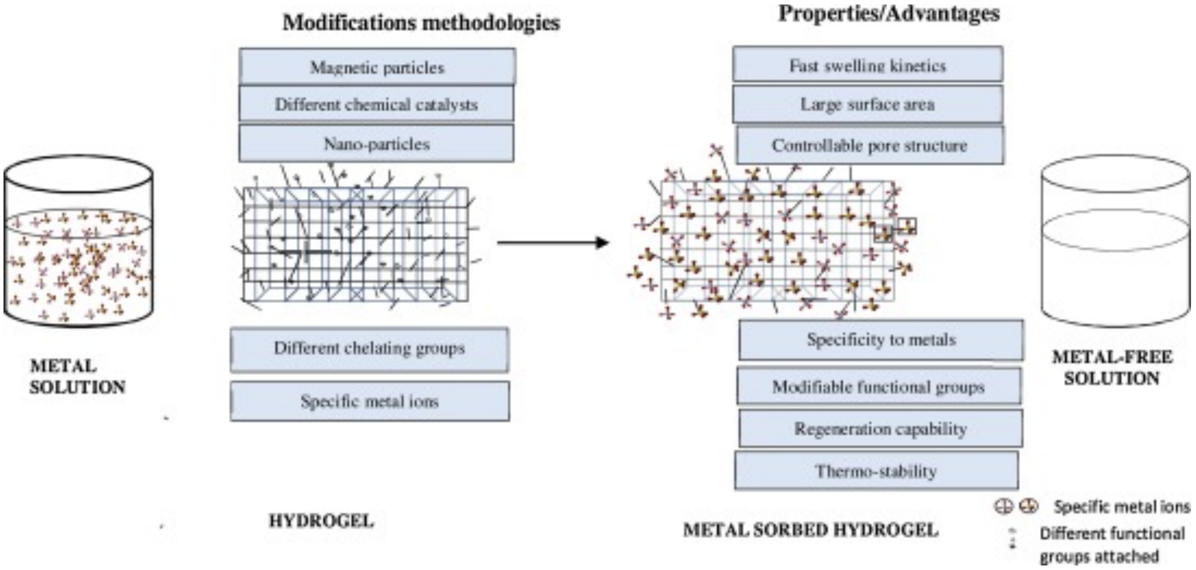


**Figure 5.** Modification methodologies and properties of hydrogels for wastewater treatment [7]

Hydrogel's metal removal efficiency is mainly attributed to the surface chemistry and the specific functional entities that are present in bulk structure of the backbone of the polymer matrix.

### 1.4.2. PVA gel beads

Polyvinyl Alcohol Hydrogel or PVA Gel is a porous hydrogel that is ideally suited for the immobilization of microorganisms. Essential for degradation of environmental pollutants. Bead’s size is around 4-5 millimeters for each bead, with micropore size, which is less than 20 microns.

PVA Gel can only be inhabited by bacteria, where neither protozoa nor metazoa cannot get inside the gel. Furthermore, more than 1 billion aerobic and anaerobic bacteria can live inside one PVA Gel bead.

In the PVA Gel system, the wastewater is mixed with oxygen in the PVA Gel Tank. The aeration process will produce sludge that contains lots of bacteria. After that, the water will be separated from the sludge in the sediment tank that produces treated water.

The bacteria have a significant role in this method. It consumes ammonia, phosphate, biological oxygen demand, and other dangerous chemical substances as its food. In addition, this process helps to clean the water for the different processes [9].

Without PVA Gel, the bacteria will be floating around uncontrollably water system and quickly goes away through the water stream. It makes the process of water treatment less effective. A high amount of excess sludge will also be produced in this situation.

When the oxygen is mixed with the wastewater inside the PVA Gel Tank, bacteria will grow. After that, PVA Gel will act as a home for those bacteria. As the bacteria grow, the process of removing dangerous chemical substances will be much more effective, and the amount of excess sludge will be reduced [9].

PVA Gel has more advantages than other media. When using other media, the bacteria only stays on the surface, but with PVA Gel, not only stays on the surface, but more importantly, the bacteria will be safe in the center of PVA Gel [28].

The shade of PVA-gel beads' surface transformed from the underlying white to yellow following 30 days of activity and develop PVA-gel dabs got red-earthy colored following 85 days, as demonstrated in Figure 6. The red-earthy colored strains are found in Figure 6 on the outside of the globules following 85 days show that the number of microorganisms joined to the PVA-gel dabs expanded with time [28]. Related investigations have discovered that when alkali nitrogen sewage is treated with PVA-gel dabs, the shade of the beads changes to red-earthy colored [29]. Consequently, it tends to be conjectured that a few strains within the PVA-gel dabs were nitrifying microbes, and this is why the cycle had high NH4 þ-N evacuation proficiency [28].

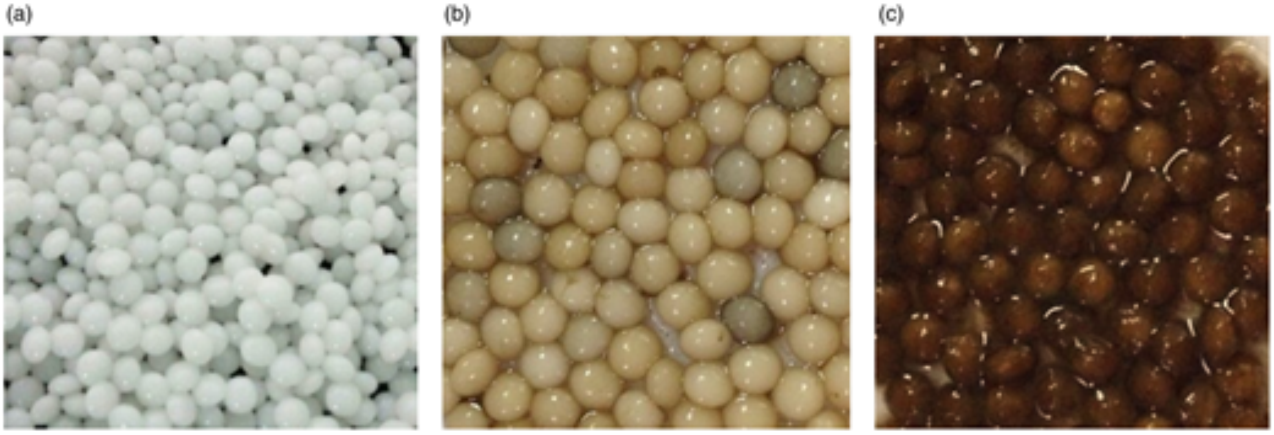


**Figure 6.** Observation of PVA-gel beads: (a) surface on day 1, (b) after 30 days, and (c) after 85 days [23]

### 1.4.3. Preparation of hydrogels

Hydrogels are made from a spectrum of natural and synthetic monomeric and polymeric units such as polyvinyl alcohol, acrylamide, starch, cellulose, alginate, gums, cellulose. HGs synthesized from natural polysaccharides have the edge over the synthetic base material since the former has advantages in bio-renewability, availability, and environment friendly. These gels consist of hydrophilic groups that become hydrated upon coming in contact with water forming a three-dimensional gel structure.

In the past decade, many alternative polymer hosts such as glass beads, silica gel, polyamine beads, alginate beads, polyvinyl alcohol, polyacrylic acid polyester have been explored for HG synthesis. These different base materials are cross-linked through different chemical (thermal, photo, or radiation-induced) or physical routes that impart a three-dimensional gel network [28].

Hydrogels rely on the idea of the polymer, were set up by two strategies for physical and compound cross-connecting. In the actual cross-connecting strategy that prompts the creation of reversible hydrogels, there are actual associations, and in the substance cross-connecting technique, there are covalent connections between the polymer chains. Cross-connected hydrogels do not break up in different solvents yet swell within sight of them [30].

Organized hydrogels have been broadly utilized in clinical and drug fields because of the absence of utilization of the cross-connecting specialist, which is harmful as a rule. Then again, compound cross-connecting techniques are viable and typical strategies for the arrangement of hydrogels [30].

The synthetic cross-connected hydrogels have better mechanical properties and solidness contrasted with the cross-connected actual hydrogels. Analysts have shown that cross-connecting levels of hydrogels increase immediate mechanical strength improvement, yet it diminishes expanding and adsorption limits by diminishing the versatility of the polymer chains. Hence, the ideal crosslinker sum ought to be resolved [30].

### 1.4.4. Physical crosslinking

Authors Mohammadzadeh and Peighambardoust, in the article *A Review on Acrylic Based Hydrogels and their Applications in Wastewater Treatment,* give information about types of physical crosslinking [30]:

- Crosslinking with hydrogen bonding

*Hydrogen bonding* is one of the methods used to generate physical crosslinking networks. Blends of polymers such as chitosan, because of the presence of the amino group in chitosan, and carboxylic group in itaconic acid and methacrylic acid, create networks with hydrogen bonding in acidic mediums. However, this bond is sensitive to pH and is deactivated by the deprotonation of the carboxylic group [30].

- Crosslinking with hydrophobic interactions

Creating crosslink bonds with *hydrophobic interactions* is a typical method for the preparation of hydrogels and micelles. One of the methods for the improvement of hydrogel's toughness is the addition of hydrophobic monomers. Researchers have shown that hydrophobic interactions between hydrophobic chains act as reversible crosslinking and effectively eliminate crack energy [30].

- Crosslinking by crystallization

In this method, formed gels with low mechanical strength and resistance are subjected to the freeze and thawing process, inducing *crystallization*. Mechanical strength and swelling of the formed gels depend on the number of cycles and the duration of each cycle [30].

- Crosslinking by ionic interactions

Physically crosslinked networks by *ionic interactions* depending on the type of used crosslinker are classified into two groups anionic and cationic [30].

### 1.4.5. Chemical crosslinking

Authors Mohammadzadeh and Peighambardoust, in the article *A Review on Acrylic Based Hydrogels and their Applications in Wastewater Treatment,* give information about types of chemical crosslinking [30]:

- Crosslinking by aldehydes

*Aldehydes*, such as formaldehyde, are used for the crosslinking of hydrogels because of their low cost and availability. Polymers with hydroxyl groups require strict conditions (low pH, high temperature) for crosslinking with aldehydes, while polymers with an amine group in their structure are crosslinked with these crosslinking agents customary conditions [30].

- Crosslinking by condensation reactions

In *condensation reactions*, two molecules that contain functional groups are combined. In addition to the large molecule production by this reaction, other side products such as water are produced [30].

- Crosslinking by free radical polymerization

One of the crosslinking methods for hydrogel preparing is free-radical *polymerization* in the vicinity of a crosslinking agent such as MBA. This method consists of three stages of initiation, propagation, and termination. This crosslinking method results in the fast preparation of hydrogel under mild conditions (room temperature and pH 7) [30].

## 1.5. Additives for PVA gel beads

In addition, both the PVA and CS are rich in active groups and can chelate metal ions, such as $Ag^+$, $Cu^{2+}$, $Zn^{2+}$, and $Fe^{2+}$ under certain conditions to form “bridges” through covalent-bonds, due to which they form more stable three-dimensional networks.

### 1.5.1. Chitosan

Chitosan is produced from of chitin, a significant component of crustacean shells and fungal biomass, and is readily available from seafood processing wastes. The chemical structures of chitin and chitosan are shown in Figure 7. Chitosan has increasingly been studied for the adsorption of various metal ions from dilute solution or wastewater [5].

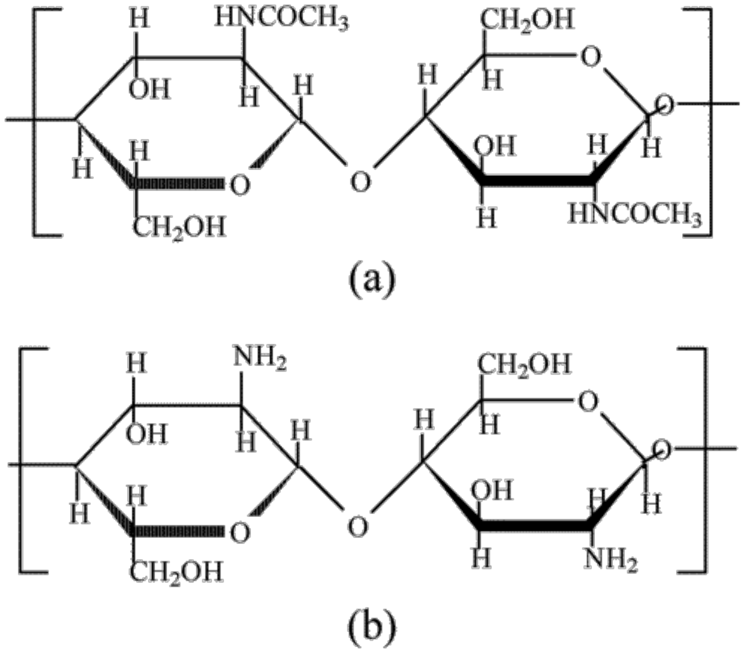


**Figure 7.** Structures of (a) chitin and (b) chitosan [5]

Chitosan is frequently utilized as drops or powder in metal adsorption. Progress has been made to deliver chitosan hydrogel dabs to recover after metal adsorption and be reused in ensuing adsorption activities. The creation of chitosan hydrogel dots includes the disintegration of chitosan pieces in an acidic corrosive arrangement followed by a precipitation cycle of infusing the chitosan arrangement in beads into a weakened sodium hydroxide arrangement. However, a considerable material limit of the hydrogel dabs is their weak synthetic opposition and mechanical strength [5].

Lately, polymer mixing has become a technique for furnishing polymeric materials with alluring viable applications. Specifically, chitosan mixed with PVA has been accounted for to have excellent mechanical and substance properties and, as a subject of incredible interest, has been broadly concentrated in the biomedical field. The upgraded property has been credited to the associations among chitosan and PVA in the mix through hydrophobic side chain total and intermolecular and intramolecular hydrogen bonds, as demonstrated in Figure 8 [5].

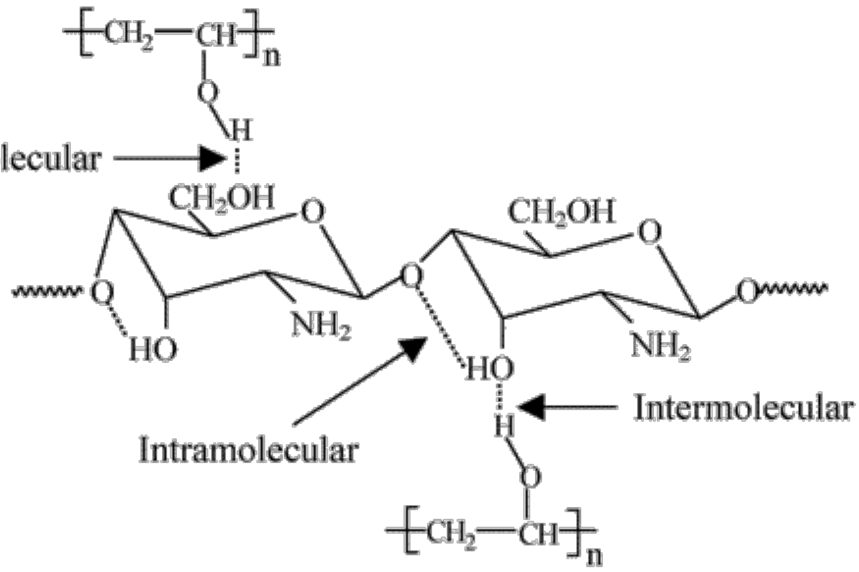


**Figure 8.** Proposed structure of PVA/CS beads showing the interactions between chitosan and PVA [5].

## 1.6. Summary of literature review

According to this scientific literature review, hydrogels are being investigated recently for wastewater treatment, and there is growing interest in hydrogels because of their excellent biocompatibility, easy preparation, and versatile applications.

PVA-Gel is a high-level wastewater treatment Bio-Carrier reasonable for civil wastewater treatment and particularly fit high BOD. Polyvinyl Alcohol Hydrogel dab has a remarkable capacity to house just the necessary miniature living beings inside its permeable construction, liable for the corruption of foreign substances, both in Nitrification and Denitrification applications. PVA-Gel has an expected 6000m$^2$/m$^3$ surface region and customers overall. Subsequently, PVA-Gel is an enormous advance in planning more modest impression plants and expanding existing office limits.

The review covered a comprehensive summary: (1) presents the mechanism of adsorption and desorption, the current knowledge on different carriers and synthesis of macroporous beads, and (2) highlights the synthesis and tailoring of specific HGs, their sorption process, and removal mechanism for specific water contaminants.

**Table 1.** Review of scientific articles.

| Gel bead type | Synthesis/origin of the beads | Pollutants removed | Removal Efficiency | Process | Wastewater | Bead size and porosity | Literature |
|---|---|---|---|---|---|---|---|
| PVA gel beads | Polyvinyl alcohol/chitosan (PVA/CS)<br>PVA/CS/Fe | COD (PVA/CS and PVA/CS/Fe performance was evaluated by monitoring the water quality parameters (COD, pH, VFA) | $RE_{COD}$=98.80% (PVA/CS)<br>$RE_{COD}$=89.68% (PVA/CS/Fe) | Anaerobic (UASB reactor was used) | Synthetic wastewater (containing inorganic medium and organic carbon (Glucose/ Alkali lignin) source) | 2-4mm, pores 30□m | [31], [32] |
| PVA gel beads | Polyvinyl alcohol (PVA) hydrogel beads crosslinked with boric acid | Nitrogen (N) | $RE_{N}$=60% | Anaerobic | Synthetic wastewater | 3-6mm | [32], [33] |
| PVA gel beads | Polyvinyl alcohol (PVA) hydrogel beads with aluminium ion on its cross-linking structure | Phosphorus (P) | | | | | [34] |
| PVA gel beads | Macroporous carrier (MPCs) post-crosslinked with glutaraldehyde | BOD, N | | Aerobic | Synthetic wastewater | 4-5mm, porosity (Ø) 1-1.6 | [35] |
| PVA hydrogel | Poly (vinyl alcohol) (PVA)/graphene oxide (GO) nano-composite hydrogels | COD | COD removal Ratio:<br>PVA ≈55.0%<br>PVA/GO 52.5%<br>PVA/GO-Glu 65.0% | Anaerobic | Industrial wastewater | 4-6mm | [36] |
| PVA gel beads | Poly(vinyl alcohol)-sodium alginate gel modified with alumina nanoparticles | Nitrogen | Ammonia nitrogen removal efficiency was 89.24% | Aerobic | Synthetic wastewater | 3.0 mm in diameter | [37] |
| PVA gel beads | Layered double hydroxide (LDH) in poly(vinylidene fluoride)/poly(vinyl alcohol) polymer | Phosphate | Removal increased as adsorbent dose increased from 5 to 50 g/L. At 8 mgP/L, percent removal increased from 47.60 to 96.93%. | | Natural water | Size ranging from 1.5 to 4.0mm with an average size of 2.4 ± 0.6 mm. | [38] |

## 2. Research methodology

The methodological part of the research project describes the research plan, presents the basic scheme of the experiment, the materials used for the production of polyvinyl alcohol gel beads, and determines the main experimental variables required for the study of sorption properties.

The research methodology is divided into the five following parts:
1. experimental plan;
2. definition of experimental variables;
3. production of polyvinyl alcohol gel beads;
4. schematic diagram of the performed experiment;
5. investigation of sorption properties of polyvinyl alcohol gel beads.

### 2.1. Experimental design of the sorption properties of polyvinyl alcohol gel beads

A plan for applying polyvinyl alcohol to micro water pollutants sorption was prepared in advance, consisting of four main stages: production of polyvinyl alcohol gel beads, modification of gel beads, sorption study, UV-VIS spectrophotometric analysis and synthetic wastewater treatment with active sludge and different types of PVA gel beads. The schematic diagram of the experiment plan is presented in Figure 9.

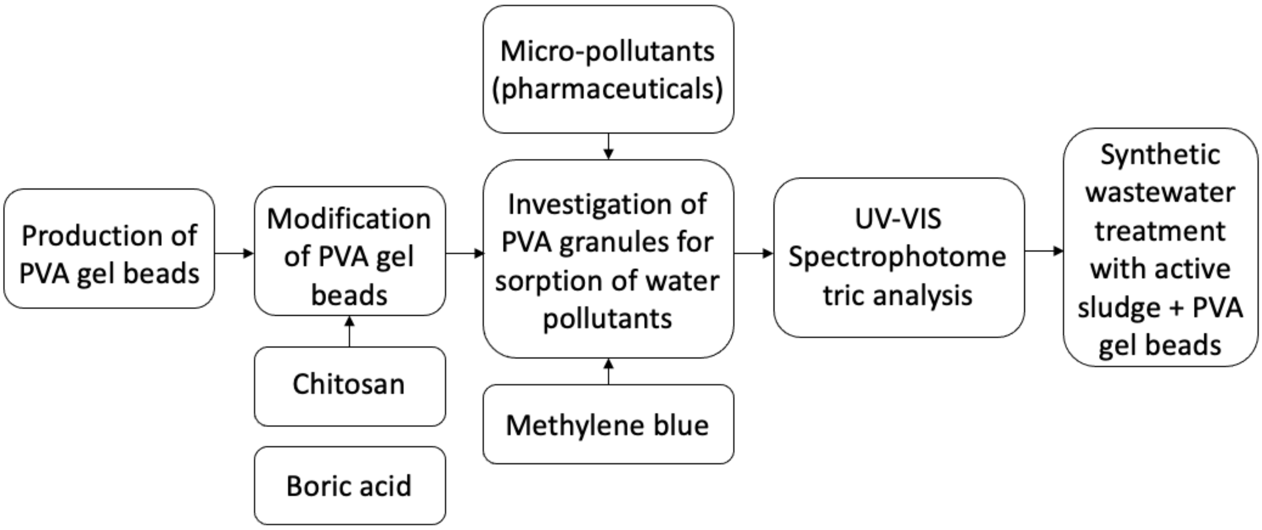


**Figure 9.** Experimental plan.

In the first stage, after analysis of the literature and recent studies, a solution is prepared from a certain amount of polyvinyl alcohol powder to produce gel beads. Then, using appropriate additives, e.g., chitosan, the gel beads are modified. In the third stage, the study of already produced gel beads for the sorption of micro water pollutants (Methylene blue, Sulfamethoxazole and Tetracycline) is performed. Finally, the UV-VIS spectrophotometric analysis method is used to analyze the experimental samples and obtain the sorption data.

The experiment uses variables for the study of sorption properties and their concentration in solution. A change over time is also observed during the study.

Polyvinyl alcohol with boric acid and polyvinyl alcohol gel beads with chitosan is prepared separately. Thus, two types of gel beads were obtained, which are further used in the sorption experiment.

Three solutions are used to study the sorption properties of the prepared gel beads: Methylene blue ($C_{16}H_{18}ClN_3S$) dye, antibiotic Sulfamethoxazole ($C_{10}H_{11}N_3O_3S$), and antibiotic Tetracycline ($C_{22}H_{24}N_2O_8$). These compounds were selected based on their relevance, frequency of use, and chemical and physical properties. The experiment is performed by varying the concentrations of Methylene blue, Sulfamethoxazole, and Tetracycline solutions: 1 mg/L, 5 mg/L, and 10 mg/L. Samples are taken at intervals of 30 and 60 minutes, respectively.

### 2.2. Synthesis of polyvinyl alcohol gel beads

After reviewing the scientific literature sources and comparing the possible production of gel beads, it was decided to produce two gel beads. The choice of hydrogel production was also strongly influenced by the pollutants removed with their help. Therefore, a decision was made to produce PVA/BA and PVA/CS gel beads and compare their sorption properties. The hydrogel production methodology is presented in the following sections.

#### 2.2.1. Production of PVA/Chitosan hydrogel beads

A 4.26 g amount of chitosan flakes was dissolved in 100 mL of dilute acetic acid (2% w/w) at 60 °C in a flask placed in a thermostatic water bath shaker stirring speed of 148 rpm for five h. An 8.51 g amount of PVA was dissolved in 100 mL of deionized (DI) water in a beaker and agitated on a magnetic stirrer (at about 800 rpm) at 80 °C for five hours [31].

The two solutions were then blended with stirring on the magnetic stirrer (at about 800 rpm) at 70 °C for 48 h, followed by another 48 h under room temperature (21−23 °C) to obtain a homogeneous gel blend [31].

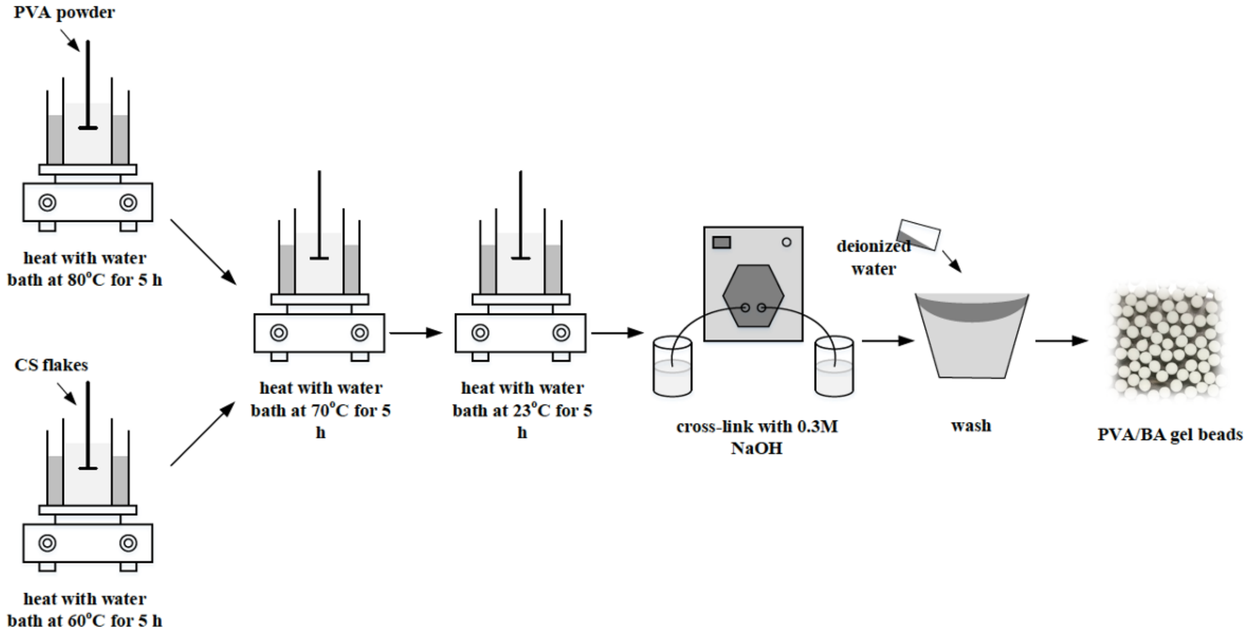


**Figure 10.** Preparation process of PVA/Chitosan gel beads

The gel blend was filtered and then introduced in droplets into a sodium hydroxide DI water solution (0.1 mol NaOH per liter DI water) through a vibration needle to form hydrogel beads with chitosan (2% w/w) and PVA (4% w/w) [31].

The hydrogel beads were thoroughly rinsed with DI water until neutral pH and were stored in DI water at room temperature before adsorption experiments. The beads were in a reasonably good spherical shape, and their diameters were in the range of 3-4 mm [31].

The production of PVA/Chitosan gel beads and the schematic diagram of the experiment are shown in Figure 10.

### 2.2.2. Production of PVA/Boric acid hydrogel beads

PVA solution was prepared by completely dissolving 12.0 g of PVA polymer powder in 100 mL of deionized water and stirring for one h under 85 °C to form a homogeneous PVA solution [4].

Then, the solution was stewed a moment at room temperature, which was followed by the addition of 5% NaOH solution (1.5 g of NaOH dissolved in 30 mL deionized water) to the above PVA solution, obtaining alkali PVA solution. After that, ultrasonication was used to remove bubbles from the alkali PVA solution [4].

The alkali PVA solution was added dropwise into the cross-linking agent (saturated boric acid solution containing 1% $CaCl_2$) via a peristaltic pump equipped with a Lange tube (ID 0.5 mm). The spherical beads were formed and stirred magnetically [4].

The gel beads were taken out carefully and washed with deionized water till pH was neutral [4].

The production of PVA/Boric acid gel beads and the schematic diagram of the experiment are shown in Figure 11.

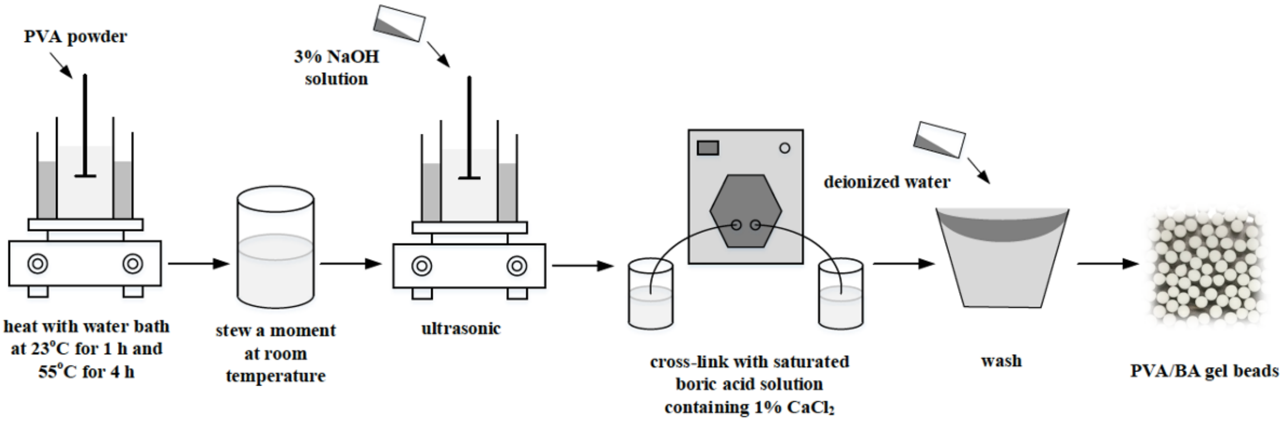


**Figure 11.** Preparation process of PVA/Boric acid gel beads.

To determine the morphological characteristics, a certain amount of gel beads is dried using a drying cabinet. The gel beads are dried at ~45°C in an oven for 24 hours [39].

After drying, the gel beads are analyzed at the Lithuanian Energy Institute. The scanning electron microscope (SEM) "S-3400N" is used to image the surface of the gel beads.

A quantity of gel beads is weighed to determine the dry mass and moisture content of the gel beads. Then, the gel beads are dried at ~45°C in a drying cabinet for 24 hours. After drying, the gel beads are weighed again. The percentage moisture content in gel beads is calculated according to the formula [40]:

$$\text{Moisture, \%} = \frac{\text{Initial mass, g} - \text{Final mass, g}}{\text{Inital mass, g}} \cdot 100\% \qquad (2.2.2.1)$$

After synthesizing the gel granules, they are washed with deionized water to neutral pH and kept in deionized water at low temperature (approx. 5°C). Then, the granules are transferred from the refrigerator to room temperature. Once a stable room temperature has been reached, the sorption study of the granules can be started [41].

## 2.3. Investigation of sorption properties of polyvinyl alcohol gel beads

Solutions of Methylene blue, Sulfamethoxazole, and Tetracycline are prepared for the sorption properties test. The initial concentrations of the Methylene blue, Sulfamethoxazole, and Tetracycline are 1 mg/L and 5 mg/L for Sulfamethoxazole, and Tetracycline; 5 mg/L and 10 mg/L for Methylene blue solutions.

To prepare the initial Methylene blue solutions, weigh an appropriate amount (5 mg and 10 mg) of Methylene blue powder, transfer to a 1 L volumetric flask, dilute to the mark with distilled water and mix thoroughly. Stock solutions of Sulfamethoxazole and Tetracycline are prepared analogously with 1 mg and 5 mg of antibiotics.

Based on the known concentrations (1 mg/L, 2 mg/L, 3 mg/L, 4 mg/L, 5 mg/L, 7.5 mg/L and 10 mg/L) of solutions of Methylene blue, Sulfamethoxazole and Tetracycline, the calibration curve is plotted to plot a calibration graph to calculate the concentration of the solution in terms of light absorption.

At room temperature, the polyvinyl alcohol gel beads are wiped with a spoon from distilled water onto a paper towel, carefully dried to remove excess water. For the spectrophotometric analysis, 10 g of each type of bead are weighed.

Using a "Spectronic Genesys 8" UV-VIS spectrophotometer, the wavelengths were determined based on the maximum sorption of a specific wavelength.

Determining the sorption wavelength of a solution is advisable to find out the wavelength that is best sorbed for each pollutant. Because the maximum wavelength absorption of a reagent from a different manufacturer may vary at different ambient temperatures, we determined the wavelength ourselves for this experiment and did not follow the scientific literature.

Spectrophotometric analysis to determine the concentration of the samples is performed using a "Spectronic Genesys 8" UV-VIS spectrophotometer. During the analysis, the sample is exposed to the light of a specific wavelength. Spectrophotometer accuracy <1nm. The light absorption of the micro-pollutant's solution is measured:

- Methylene blue at 661 nm;
- Sulfamethoxazole at 258 nm;
- Tetracycline at 357 nm.

Micro-pollutants sorption test procedure:

1. Add 250 ml of the prepared 10 mg/L Methylene blue solution to a 300 ml Erlenmeyer flask.
2. Place the flask containing the solution on a magnetic stirrer and set the stirring speed at ~490 rpm.
3. Weigh 10 g of gel beads into the solution.
4. Samples are taken every 30, 60, 120, 180, 240, and 300 minutes, adsorption is performed for 300 minutes. A disposable pipette and a 1 cm diameter disposable plastic cuvette are used for sampling.
5. Measure light absorption for all samples (blank sample – dionised water).

The experiment is performed by varying the concentration of Methylene blue solution and the type of gel beads.

The test is repeated analogously with micro-pollutants solutions of Sulfamethoxazole and Tetracycline. The obtained data are analyzed using adsorption and reaction kinetics models.

### 2.3.1. Adsorption and kinetic models

The adsorption experimental data was fitted with the Freundlich and Langmuir adsorption models whose non-linear and linear equations are described in Table 2. In addition, constants required for accurate comparison of PVA gel beads were obtained from the plots by picking certain slope and intercept values.

Langmuir's and Freundlich's adsorption equilibrium models are used to determining sorption capacity. Langmuir adsorption isotherm quantifies the formation of an adsorbate monolayer on the outer surface of the adsorbent. Langmuir isotherm takes place in a monolayer on surfaces with a finite number of active centers. When the active center adsorbs the molecule, it becomes inactive, and adsorption no longer occurs. The Freundlich isotherm is used to describe the adsorption characteristics of heterogeneous surfaces [42].

**Table 2.** Langmuir and Freundlich adsorption models [42].

| **Name** | **Non-linear form** | **Linear form** | **Plot** | **Slope** | **Intercept** |
|---|---|---|---|---|---|
| Langmuir | $q_e = \frac{Q_m \cdot K_L \cdot c_e}{1 + K_L \cdot Q_m}$ | $\frac{c_e}{q_e} = \frac{1}{K_L \cdot Q_m} + \frac{c_e}{Q_m}$ | $\frac{c_e}{q_e}$ vs. $c_e$ | $\frac{1}{Q_m}$ | $\frac{1}{K_L \cdot Q_m}$ |
| Freundlich | $q_e = K_F \cdot c_e^{\frac{1}{n}}$ | $\log q_e = \log K_F + \frac{1}{n} \log c_e$ | $\log q_e \; vs \log c_e$ | $\frac{1}{n}$ | $\log K_F$ |

Where:

$q_e$ is the amount of the adsorbate adsorbed per gram of the adsorbent after reaching equilibrium (mg/g);

$c_e$ denotes the substrate concentration in the liquid after reaching equilibrium (mg/L);

$K_F$ is Freundlich constant, the adsorption capacity of the adsorbent (mg/g (L/mg)1/n);

$n$ is Freundlich constant indicating the adsorption favourability;

$Q_m$ represents the maximum adsorption capacity required to form the monolayer on the surface of the adsorbent (mg/g);

$K_L$ is Langmuir constant related to the affinity of the binding sites (L/mg).

The amount of the adsorbed substrate at the equilibrium state (qe) was calculated by using the following equation:

$$q_e = \frac{(c_0 - c_t) \cdot V}{m} \tag{2.3.1.2}$$

Where:

$C_0$ represents the initial solute concentration in the liquid phase (mg/L);

$C_e$ denotes the solute concentration in the liquid phase after reaching equilibrium (mg/L);

$V$ is the volume of the solution (L);

$M$ stands for the dry mass of the adsorbent (g).

The pseudo 1st and pseudo 2nd order kinetic models were used to describe the micro-pollutants adsorption on different PVA gel beads. The linear and non-linear forms of model equations can be found in a Table 3.

**Table 3.** Pseudo first and pseudo second order kinetic models [42].

| **Name** | **Non-linear form** | **Linear form** | **Plot** | **Constants** |
|---|---|---|---|---|
| 1st order | $q_t = q_e(1 - exp^{-k_1 \cdot t})$ | $\log(q_e - q_t) = \log(q_e) - \frac{k_1 \cdot t}{2.303}$ | $\log(q_e - q_t)$ vs. t | $k_1$ = 2.303 ·S |
| 2nd order | $q_t = \frac{k_2 \cdot q_e^2 \cdot t}{1 + k_2 \cdot q_e \cdot t}$ | $\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t$ | $\frac{t}{q_t}$ vs. t | $q_e = \frac{1}{S}$; $k_2 = \frac{S^2}{L}$ |

S – slope; L – intercept

where:

$q_e$ is the amount of adsorbate adsorbed per gram of the adsorbent after reaching equilibrium (mg/g);

$q_t$ represents the amount of adsorbate adsorbed per gram of the adsorbent (mg/g) during time t (h);

$k_1$ denotes the pseudo 1st order rate constant (1/h);

$k_2$ represents the pseudo 2nd order rate constant (g/mg·h).

The data fitting to one of these models can define which adsorption process is leading. The pseudo 1st order model indicates that the reaction is linked to physisorption, while pseudo 2nd order kinetics covers up chemisorption process [42].

## 2.4. Synthetic wastewater treatment with active sludge and PVA gel beads

The adsorption experiments and biomass washing were carried out in phosphate buffered saline (PBS). The pH was checked at the start, during and at the end of each experiment; in all experiments the pH remained between 6.7 and 7.4 [43].

Synthetic wastewater consisted of phosphate saline buffer, nutrients, and trace elements solutions. In addition, glucose ($C_6H_{12}O_6$) was used as an organic carbon source.

**Table 4.** Composition of phosphate saline buffer [43].

| Chemical compound | Formula | Concentration |
|---|---|---|
| Sodium chloride | $NaCl$ | 800 mg·L$^{-1}$ |
| Potassium chloride | $KCl$ | 20 mg·L$^{-1}$ |
| Disodium phosphate | $Na_2HPO_4$ | 144 mg·L$^{-1}$ |
| Monopotassium phosphate | $KH_2PO_4$ | 24 mg·L$^{-1}$ |

The biomass, used as inoculum, was stored in PBS supplemented with nutrients.

**Table 5.** Composition of nutrients used for biomass inoculum [43].

| Chemical compound | Formula | Concentration |
|---|---|---|
| Ammonium chloride | $NH_4Cl$ | 170 mg·L$^{-1}$ |
| Calcium chloride dihydrate | $CaCl_2 \cdot 2H_2O$ | 8 mg·L$^{-1}$ |
| Magnesium sulfate heptahydrate | $MgSO_4 \cdot 7H_2O$ | 9 mg·L$^{-1}$ |
| Trace element's solution | | 1 ml/L |

**Table 6.** Composition of trace element's solution [43].

| Chemical compound | Formula | Concentration |
|---|---|---|
| Iron (III) chloride tetrahydrate | $FeCl_3 \cdot 4H_2O$ | 2000 mg·L$^{-1}$ |
| Cobalt (II) chloride hexahydrate | $CoCl_2 \cdot 6H_2O$ | 2000 mg·L$^{-1}$ |
| Manganese (II) chloride tetrahydrate | $MnCl_2 \cdot 4H_2O$ | 500 mg·L$^{-1}$ |
| Copper (II) chloride dihydrate | $CuCl_2 \cdot 2H_2O$ | 30 mg·L$^{-1}$ |
| Zinc chloride | $ZnCl_2$ | 50 mg·L$^{-1}$ |
| Boric acid | $H_3BO_3$ | 50 mg·L$^{-1}$ |
| Ammonium paramolybdate tetrahydrate | $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ | 90 mg·L$^{-1}$ |
| Sodium selenite pentahydrate | $Na_2SeO_3 \cdot 5H_2O$ | 100 mg·L$^{-1}$ |
| Nickel (II) chloride hexahydrate | $NiCl_2 \cdot 6H_2O$ | 50 mg·L$^{-1}$ |

Everyday active sludge was supplemented with phosphate saline buffer, nutrients, trace elements, and 500 mg/L glucose solutions. Samples for parameter analysis were taken daily.

The reactor volume was filled with 10% gel beads (PVA/CS and PVA/BA). The volume of the reactors used in this study was 300 mL each.

The PVA/CS and PVA/BA gel beads were stirred in the reactor with the help of a magnetic stirrer (aprox. 190 rpm). The activated sludge was aerated throughout the study. Samples were taken with a 50 mL syringe for analysis.

Studies of synthetic wastewater treatment with active sludge and PVA gel beads were performed using Hanna multiparameter photometer HI-8339 and reagents for specific parameter (phosphate, nitrate, amonia, total nitrogen, total phosphorus).

Studies of total organic compound in synthetic wastewater treatment with active sludge and PVA gel beads were performed using Total Organic Carbon Analyzer (TOC), Shimadzu, TOC-L.

The study used five reactors that were filled with wastewater and:

1. 50 mL active sludge;
2. 50 mL active sludge and PVA/CS gel beads (10% of reactor volume);
3. 50 mL active sludge and PVA/BA gel beads (10% of reactor volume);
4. PVA/CS gel beads (10% of reactor volume);
5. PVA/BA gel beads (10% of reactor volume).

During the experiment, when synthetic wastewater were treated with active sludge and PVA gel beads, parameters were measured:

- total nitrogen (TN);
- total phosphorus (TP);
- total organic carbon (TOC);
- nitrates ($NO^{3-}$);
- phosphates ($PO_4^{3-}$);
- ammonia ($NH_3$).

## 3. Research results and discussion

This section describes the structure, surface morphology, and size of the produced polyvinyl alcohol gel beads. Also, the sorption results of Methylene blue, Sulfamethoxazole, and Tetracycline are presented. The dependences of the used adsorbent (two types of polyvinyl alcohol gel beads) and the contaminant concentration have been determined. The sorption capacity of the modified polyvinyl alcohol gel beads for Methylene blue dye, Sulfamethoxazole, and Tetracycline was calculated using the Lengmuir and Freundlich isotherm models, and the adsorption reaction rates were determined from the adsorption kinetics models.

### 3.1. Characterization of PVA gel beads

### 3.1.1. Morphologies and porous structure of PVA gel beads

Polyvinyl alcohol with chitosan and polyvinyl alcohol with boric acid gel beads were produced and further used in the studies. Some of the gel beads were used to determine morphological properties. The diameter of the wet gel beads was determined using an electronic caliper. 50 beads measuring 3.9 ± 0.09 mm were measured.

Photographs of the surface structure of the dried gel beads were taken at the Lithuanian Energy Institute using a Scanning electron microscope "S-3400N". Photos were taken at different magnifications. Figure 12 surface structure photographs of polyvinyl alcohol with chitosan and polyvinyl alcohol with boric acid are presented. Photos magnified 35-60 times.

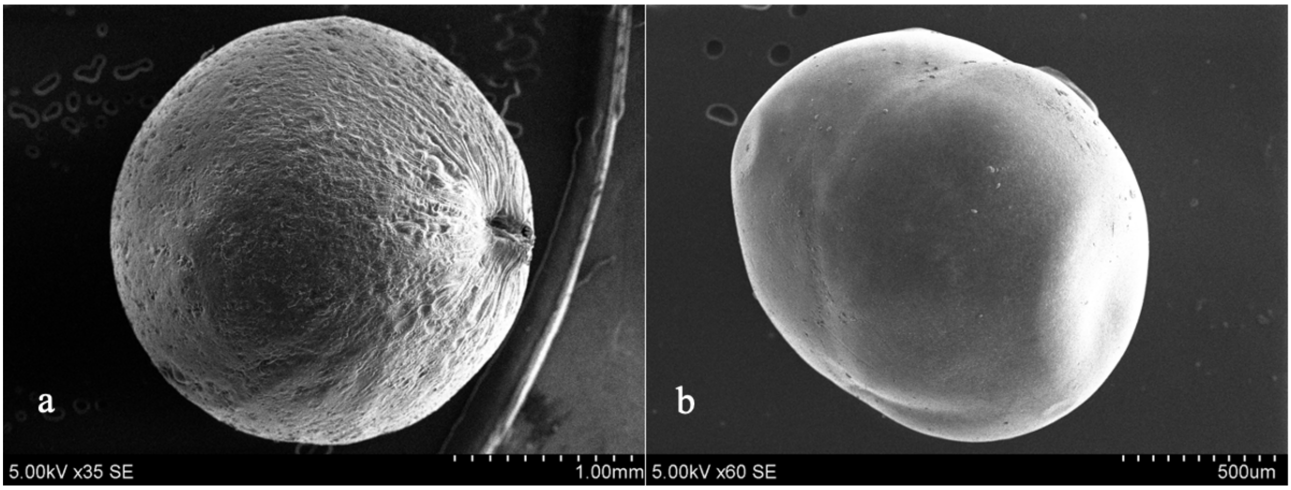


**Figure 12.** Surface structure photographs of polyvinyl alcohol with boric acid (a) and polyvinyl alcohol with chitosan (b) (photos magnified 35-60 times)

The photos were taken at 100x and 1000x times. Gel beads of polyvinyl alcohol with boric acid (Figure 13 a) have an uneven surface that is irregular in shape. The surface of the dried polyvinyl alcohol with chitosan gel beads (Figure 13 b) is smooth and solid, with bumps of various sizes spread over the entire surface area. Gel beads of polyvinyl alcohol with chitosan have a smoother and more stable surface, evenly distributed than boric acid. Figure 13 shows photographs of the surface structure of the dried gel beads. Photos are magnified 100 times, and photos in the upper corners are magnified 1000 times. The beads are fixed within the measuring range of millimeters.

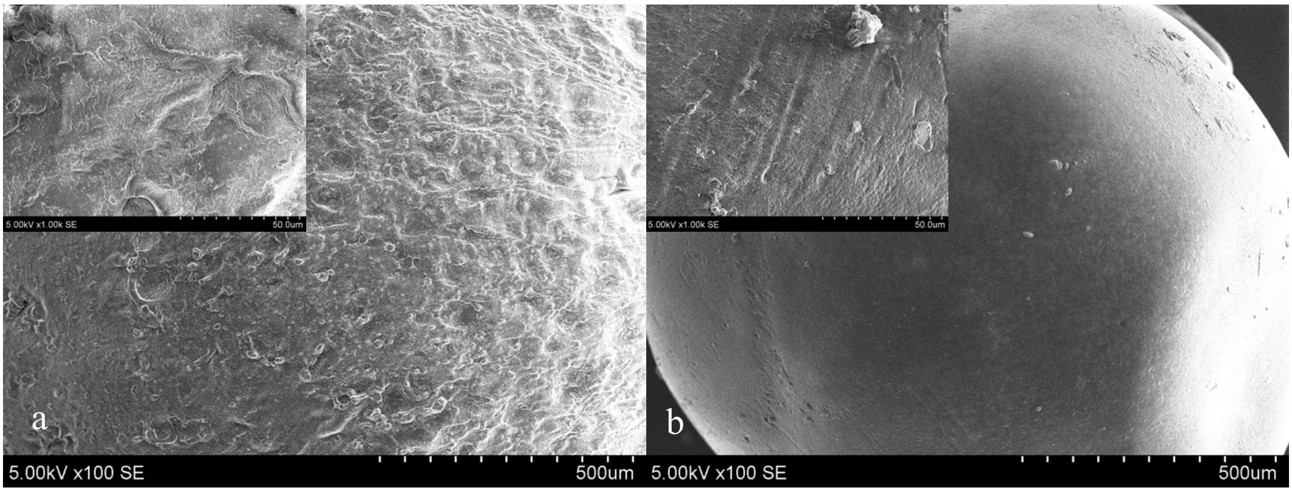


**Figure 13.** Surface structure photographs of polyvinyl alcohol with boric acid (a) and polyvinyl alcohol with chitosan (b) (photos magnified 100 and 1000 times)

PVA/CS and PVA/BA gel beads with diameters of 3-4mm were successfully synthesized. As shown in the inset of Fig. 14 and Figure 15, both PVA/CS and PVA/BA gel beads showed smooth surfaces. PVA/CS and PVA/BA gel beads were after the sorption of Methylene blue. After the synthesis, the PVA/CS and PVA/BA gel beads exhibited ivory color according to the microscope photos (Figure 14 and Figure 15), both the PVA/CS and PVA/BA gel beads showed rough, non-ordered, and well-developed porous structure, which created favorable habitat for microbes.

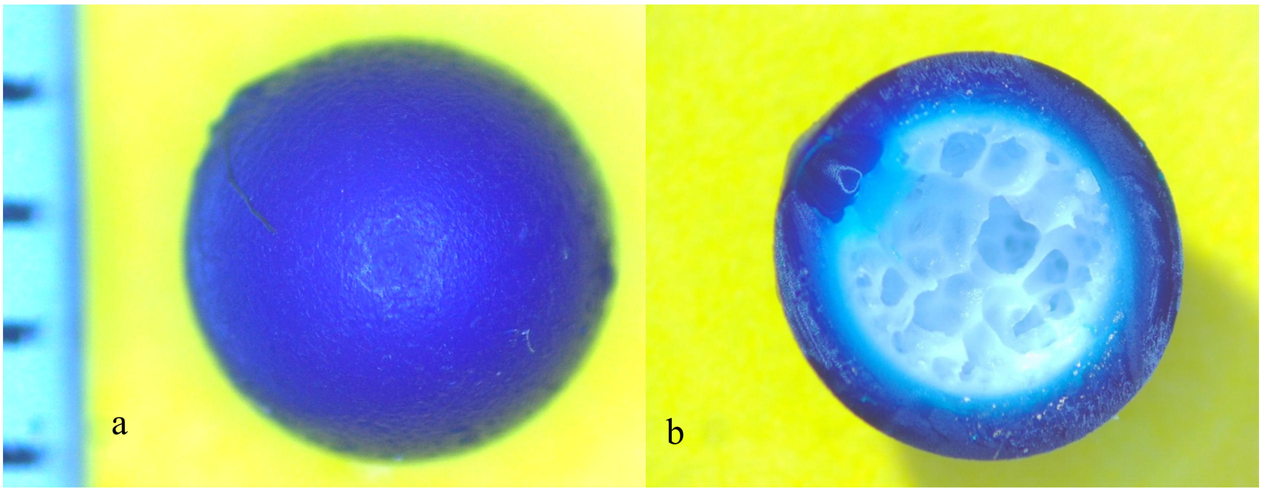


**Figure 14.** Polyvinyl alcohol with boric acid gel beads surface (a) and porous structure (b).

Two types of PVA beads were obtained during the synthesis. In Figure 14a and Figure 15a, we can see pictures of PVA/CS and PVA/BA beads taken with a microscope. Their appearance and size are very similar, but the main differences are seen in Figure 14b and Figure 15b, which show the porosity of the gel beads. The photos show the porous gel bead structure; PVA/BA is characterized by larger pores suitable for establishing microorganisms. In addition, studies have shown a difference in the mechanical properties of these gel beads.

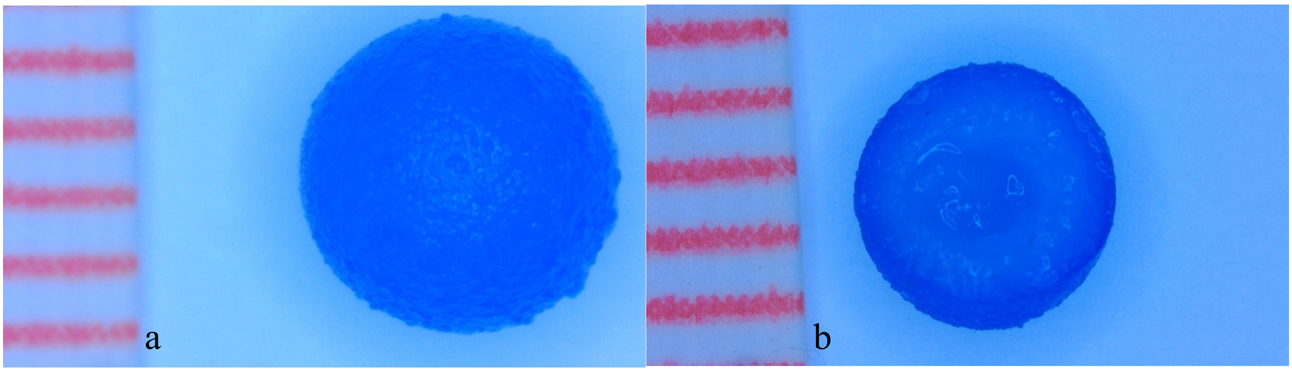


**Figure 15.** Polyvinyl alcohol with chitosan gel beads surface (a) and porous structure (b).

PVA/CS has poor chemical resistance and mechanical strength, while PVA/BA has Strong stability for long-term use.

### 3.1.2. FTIR analysis of PVA gel beads

FTIR spectra of pure PVA gel beads were obtained to identify the functional groups after the cross-linking process.

FTIR spectra of pure PVA powder, PVA/CS, and PVA/BA were obtained to identify the change in functional groups before and after the cross-linking process. For pure PVA FTIR spectra we have used data from literature source [4].

For pure polyvinyl alcohol powder, the most prominent characteristic peak was the symmetric stretching vibrations of O–H centered at 3278 $cm^{-1}$. The C–O area of PVA was at 1144 and 1096 $cm^{-1}$, respectively. The C–C stretching vibrations for the amorphous sequence of PVA were located at 848 $cm^{-1}$, and the absorption corresponding to the C–H stretching occurred at 1376 $cm^{-1}$. Absorption bands around 1740, 1558, and 1260 $cm^{-1}$ respectively corresponded to C=O, =C, and C–O–C in the remaining acetyl groups from the precursor polymer of PVA [4].

Compared with FTIR of pure PVA, the spectra PVA/BA (Figure 16) demonstrated that the absorbance peak of C–H shifted to a higher wavelenght (from 1376 to 1438 $cm^{-1}$), which can be attributed to the formation of sodium alcoholate structure in alkali PVA. Also, the band at 945 $cm^{-1}$ derived from O–H out-of-plane deformations left shifted to 838 $cm^{-1}$ with the incorporation of NaOH solution. The shift to low wave number indicates that the intermolecular hydrogen bonds in PVA were weakened, which may be because the incorporated inclusions (NaOH) strongly interacted with the PVA molecules; thus, interfering with the interactions among PVA molecules [4].

Furthermore, the bending band from O–Na groups located at 665 $cm^{-1}$ also showed a significant difference, suggesting that more cross-linking points are available for further reactions. With the addition of boric acid, two novel peak at 1342 $cm^{-}1$ appeared, which can be attributed to the B–O–C bending [4].

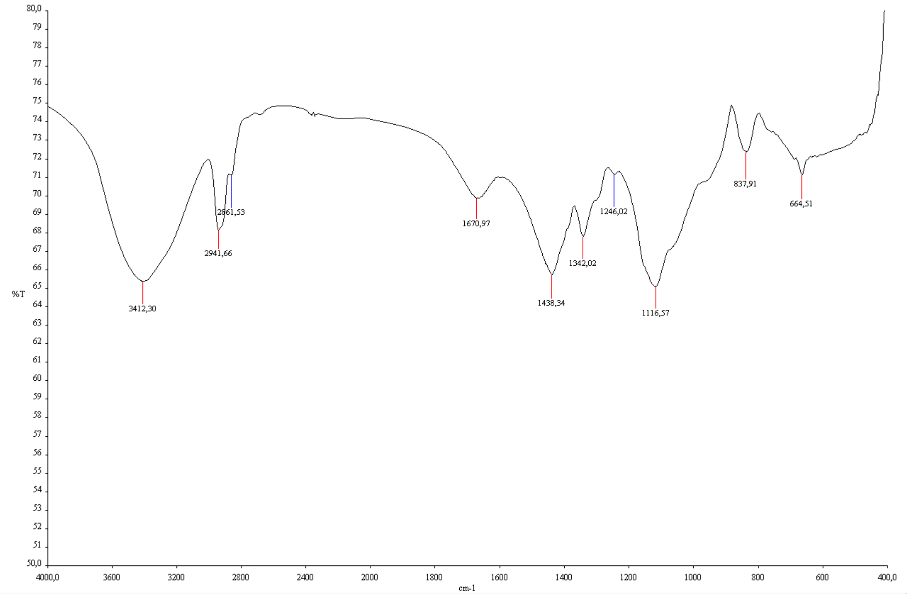


**Figure 16.** FTIR analysis of the PVA/BA gel beads

Using FTIR spectra in transmission mode from powders, the functional groups of CS, PVA, and PVA/CS gel beads and were identified (Figure 17) [31].

For chitosan, a strong absorption peak observed at 3436 cm$^{-1}$ was attributed to hydroxyl (O-H) stretching vibration. The peak at 2923 cm$^{-1}$ was the overlapping of O-H and N-H stretching vibrations, confirming the existence of intermolecular hydrogen bond. The absorption peaks of -NH$_2$ around 1092 cm$^{-1}$ were characteristic of chitosan and assigned to amide I (1460 and 1430 cm$^{-1}$), amide (1320 and 1157 cm$^{-1}$) [31].

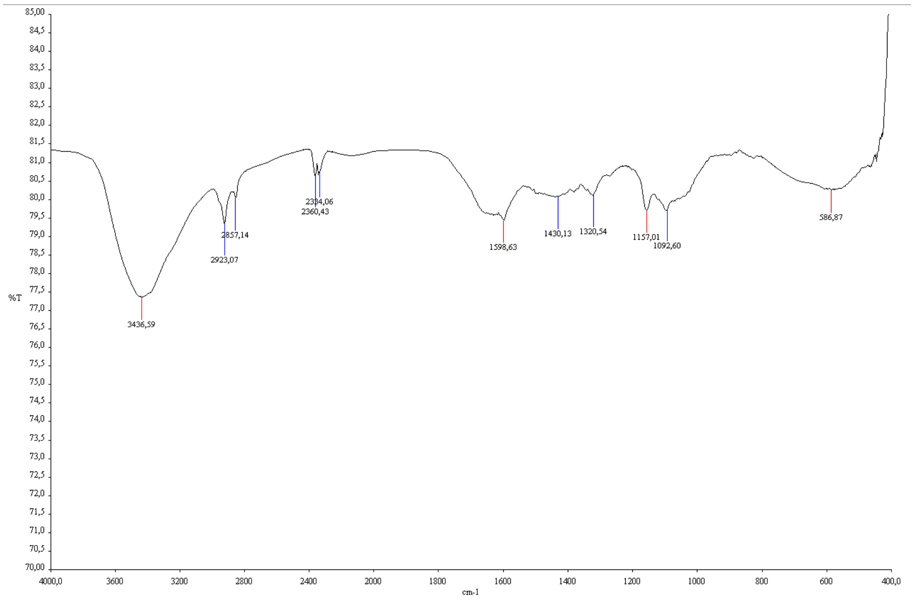


**Figure 17.** FTIR analysis of the PVA/CS gel beads

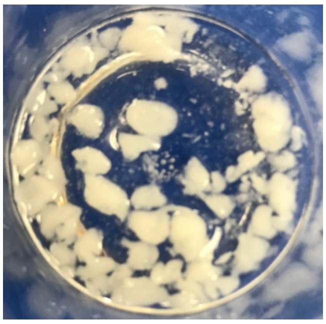
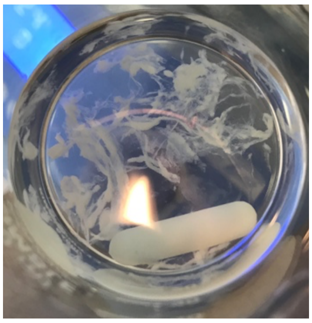
## 3.2. Synthesis of Polyvinyl alcohol geal beads

The synthesis of PVA gel beads posed more challenges than expected. In this chapter, information about different syntheses of PVA conditions will be presented.

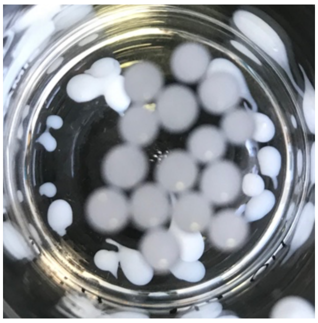
During the production of the granules, several different granule synthesis methods had to be tried, and changes were made to form the granules with good mechanical strength and regular shape.

The Table 7 presents the systematic polyvinyl alcohol/boric acid gel beads synthesis methodologies. Different types of synthesis were tested to select the most suitable synthesis for the production of granules. In addition, different materials, reagents, and crosslinking solutions were also tested during the study. All this was done on the basis of scientific literature and in order to select the best synthesis conditions for the production of granules.

**Table 7.** Synthesis conditions of Polyvinyl alcohol geal beads with chitosan.

| **Synthesis conditions** | | **Cross-linking agent** | **Comments** | **Photo** |
|---|---|---|---|---|
| **Preparation of the solutions** | **Homogenization** | | | |
| Solutions of 10% (w/v) PVA and 3.3% (w/v) CS were separately dissolved in equal volumes of acetic acid solutions (2.5%, v/v). | The PVA solution and CS solution were mixed together and stirred for 0.5 h to form homogeneous PVA/CS solutions. | 5% (w/v) NaOH | No granules formed. There were formations in an irregular shape. Partially dissolved Chitosan particles were visible.<br>Needles of various inner diameters were tried, but this did not help.<br>The granules were formed by dripping into a solution without stirring and into a solution with a magnetic stirrer. |  |
| Chitosan flakes was dissolved in 100 mL of dilute acetic acid (2% w/w) at 60 °C in a flask placed in a thermostatic water bath shaker with a stirring speed of 148 rpm for 5 h.<br>PVA was dissolved in deionized (DI) water in a beaker and agitated on a magnetic stirrer (at about 800 rpm) at 80 °C for 5 h. | The two solutions were then blended together with stirring on the magnetic stirrer (at about 800 rpm) at 70 °C for 48 h, followed by another 48h under room temperature (21-23 °C) to obtain a homogeneous gel blend. | The gel blend was introduced in droplets into a NaOH-methanol solution (0.1 mol NaOH per litre methanol) through a needle using peristaltic pump to form hydrogel beads. | No granules formed. In the crosslinking solution, only threads formed, which did not strengthen even after some time.<br>Needles of various inner diameters were tried. |  |

| **Synthesis conditions** | | **Cross-linking agent** | **Comments** | **Photo** |
|---|---|---|---|---|
| **Preparation of the solutions** | **Homogenization** | | | |
| PVA was dissolved in deionized water (80 °C, 5h)<br>CS was dissolved 2% acetic acid (60 °C, 5h) | PVA and CS homogenization for 48 h (70 °C) and 48 h (23 °C) | PVA/CS granules are formed in 0.1 M NaOH-methanol | The synthesis was carried out as before, but the Chitosan flakes, were crushed with a mortar, and Chitosan was treated with more vigorous acetic acid. Formation improved slightly, but the granules did not form and settled and adhered to the bottom. |  |
| Chitosan has been changed from a technical one to a new.<br>TCI chemicals CAS RN: 9012-76-4 \| Product Number: C0831<br>Chitosan (200-600mPa·s, 0.5% in 0.5% Acetic Acid at 20°C) | | | | |
| PVA was dissolved in deionized water (80 °C, 5h)<br>CS was dissolved 2% acetic acid (60 °C, 5h) | PVA and CS homogenization for 48 h (70 °C) and 48 h (23 °C) | PVA/CS granules are formed in 0.1 M NaOH-methanol | Replacing technical chitosan with a new one showed an apparent improvement in CS solubility.<br>The granules were still very difficult to form and had an irregular shape (they had a “tail” that would appear when the granules in the crosslinking solution fell towards the bottom). |  |

| **Synthesis conditions** | | **Cross-linking agent** | **Comments** | **Photo** |
|---|---|---|---|---|
| **Preparation of the solutions** | **Homogenization** | | | |
| PVA was dissolved in deionized water (80 ℃, 5h)<br>CS was dissolved 2% acetic acid (60 ℃, 5h | PVA and CS homogenization for 48 h (70 ℃) and 48 h (23 ℃) | PVA/CS granules are formed in:<br>- 0.1 M NaOH-methanol<br>- 0.2 M NaOH-methanol<br>- 0.3 M NaOH-methanol<br>- 0.1 M NaOH-aqueous solution<br>- 0.2 M NaOH-aqueous solution<br>- 0.3 M NaOH-aqueous solution | - 0.1 M NaOH-methanol: as in previous experiments, the granules formed poorly.<br>- 0.2 M NaOH-methanol: granules formed but were very unstable and irregular in shape.<br>- 0.3 M NaOH-methanol: poorly formed, irregular shape, with “tail.”<br>- 0.1 M NaOH-aqueous solution: granules form but are not strong enough.<br>- 0.2 M NaOH-aqueous solution: granules are formed. After 5 min of rotation with a magnetic bag.<br>- 0.3 M NaOH-aqueous solution: the strongest granules of all, not even torn by a magnetic stirrer. | <br>0.2 M NaOH-methanol<br><br>0.3 M NaOH- aqueous |

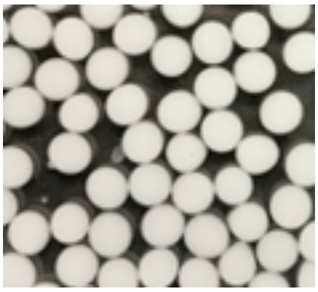
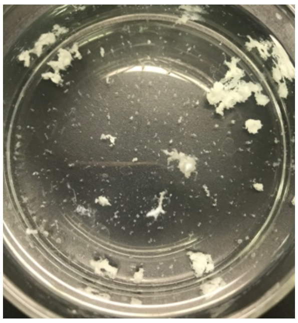
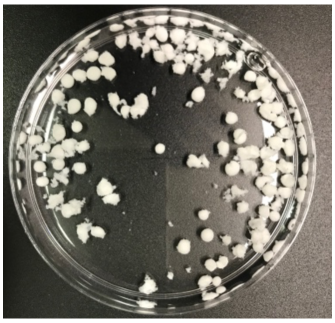
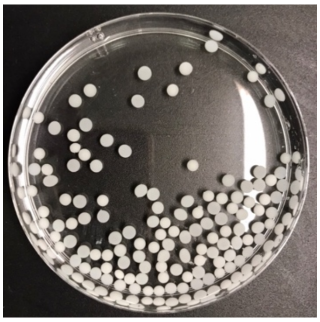
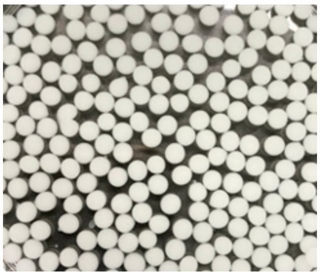
| **Synthesis conditions** | | **Cross-linking agent** | **Comments** | **Photo** |
|---|---|---|---|---|
| **Preparation of the solutions** | **Homogenization** | | | |
| PVA was dissolved in deionized water (80 °C, 5h)<br>CS was dissolved 2% acetic acid (60 °C, 5h) | PVA and CS homogenization for 48 h (70 °C) and 48 h (23 °C) | 5% NaOH aqueous solution | PVA / CS granules are formed in 0.3 M NaOH aqueous solution with a peristaltic pump, which was equipped with a needle (ID 0.838 mm)<br>1.2-1.5 rpm<br>The granules were mechanically solid and stable. |  |

Table 8 presents the systematic polyvinyl alcohol/chitosan gel beads synthesis methodologies. Different types of synthesis were tested to select the most suitable for the gel beads production. In addition, during the study, different materials, reagents, concentrations of crosslinking solutions, and PVA dissolution temperatures were also tested. All this was done based on scientific literature and to select the best synthesis conditions for the production of gel beads. Table 8 presents the fundamental conditions for synthesis, homogenization, and crosslinking. Comments and photos are also provided for each type of synthesis.

**Table 8.** Synthesis conditions of Polyvinyl alcohol geal beads with boric acid.

| **Synthesis conditions** | | **Cross-linking agent** | **Comments** | **Photo** |
|---|---|---|---|---|
| **Preparation of the solutions** | **Homogenization** | | | |
| 12.0 g of PVA polymer powder in 100 mL of deionized water and stirring for 1 h under 85 ℃ to form homogeneous PVA solution. | The solution was stewed a moment at room temperature, which was followed by addition of 5% NaOH solution to the above PVA solution, obtaining alkali PVA solution | Cross-linking agent (saturated boric acid solution containing 1% $CaCl_2$) | The granules did not form at all. Only those that fell into the solution ruptured and spread on the surface.<br>The granules did not even form; it appeared that the PVA was completely undissolved. |  |
| 12.0 g of PVA polymer powder in 100 mL of deionized water and stirring for 5 h under 85 ℃ to form homogeneous PVA solution. | The solution was stewed a moment at room temperature, which was followed by addition of 5% NaOH solution to the above PVA solution, obtaining alkali PVA solution | Saturated boric acid solution containing:<br>- 2.5 % $CaCl_2$<br>- 5.0 % $CaCl_2$<br>- 7.5 % $CaCl_2$<br>- 10.0 % $CaCl_2$ | - 2.5% CaCl2 granules formed but were not stable.<br>- 5.0% $CaCl_2$ granules formed but in a very irregular shape.<br>- 7.5% $CaCl_2$ granules did not form<br>- 10.0% $CaCl_2$ granules did not form |  |
| 12.0 g of PVA polymer powder in 100 mL of deionized water and stirring for 5 h under 85 ℃ to form homogeneous PVA solution | The solution was stewed a moment at room temperature, which was followed by addition of 5% NaOH solution to the above PVA solution, obtaining alkali PVA solution | Cross-linking agent (saturated boric acid solution containing 1% $CaCl_2$) | It was decided that PVA should be dissolved for a longer period (5 hours). The granules formed a solid, same size. |  |
| 12.0 g of PVA polymer powder in 100 mL of deionized water and stirring for 1h under room temperature. After that 5 h under 55 ℃ to form homogeneous PVA solution | The solution was stewed a moment at room temperature, which was followed by addition of 5% NaOH solution to the above PVA solution, obtaining alkali PVA solution | Cross-linking agent (saturated boric acid solution containing 1% $CaCl_2$) | The granules are mechanically very strong, of uniform size (3-4 mm). |  |

### 3.3. Results of the study of sorption properties of PVA gel beads with Methylene blue

To prepare the calibration curve, prepare solutions of different concentrations of Methylene blue by the dilution method and measure light absorption at 661 nm (Table 9).

**Table 9.** Concentration dependence of adsorption of Methylene blue solution

| Concentration, mg/L | Absorbtion |
|---|---|
| 1,0 | 0,247 |
| 2,0 | 0,501 |
| 3,0 | 0,752 |
| 4,0 | 0,998 |
| 5,0 | 1,247 |
| 7,5 | 1,761 |
| 10,0 | 2,174 |

From the known concentrations of the solution, a calibration graph (Figure 18) is drawn, from which the unknown concentrations will be determined later.

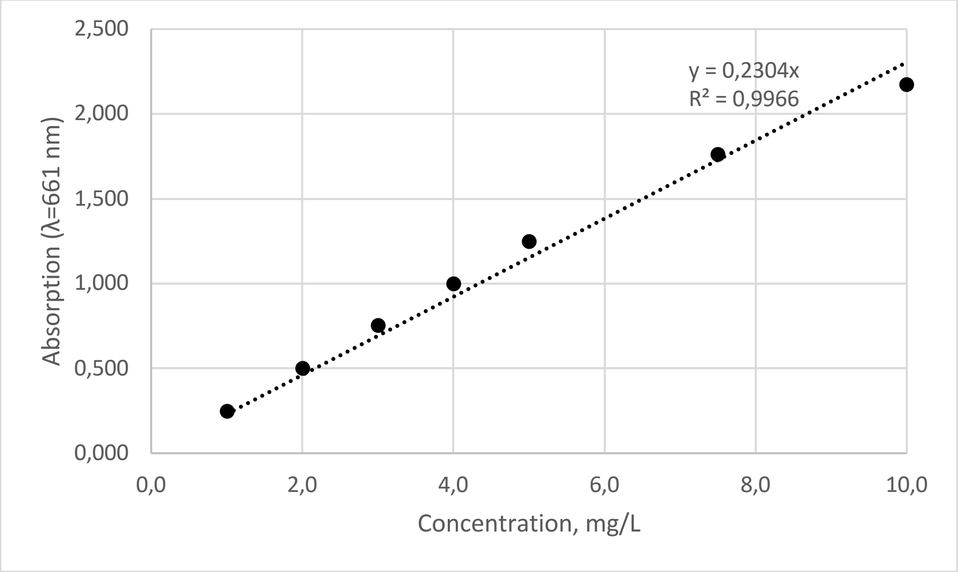


**Figure 18.** Concentration dependence of adsorption of Methylene blue solution

Stock solutions of Methylene blue were used for the sorption properties: 10 mg/L; 7.5 mg/L; 5 mg/L; 4 mg/L, 3 mg/L, 2 mg/L, 1 mg/L. Polyvinyl alcohol gel beads with boric acid and polyvinyl alcohol gel beads with chitosan are used as adsorbents in the study.

The light adsorption of Methylene blue solution of polyvinyl alcohol gel beads at 661 nm is measured. Initial Methylene blue concentrations are 10 mg/L and 5 mg/L. Sorption is performed for 180 min, samples are measured at 30, 60, 120, 180, 240, and 300 min. interval. 250 ml of each concentration solution and 10 g of dried gel beads of each type are used for the experiment. The variation of Methylene blue concentration with time and the adsorbent used is shown in Table 10. The concentration was calculated from the calibration curve (Figure 18).

**Table 10.** Dependence of Methylene blue concentration on sorption time and adsorbent

| Gel beads | Pollutant solution | 0 min | 30 min | 60 min | 120 min | 180 min | 240 min | 300 min |
|---|---|---|---|---|---|---|---|---|
| PVA/CS | 10 mg/L Methylene blue | 9,401 | 8,164 | 7,487 | 7,166 | 4,258 | 3,611 | 3,220 |
| | 5 mg/L Methylene blue | 4,965 | 2,188 | 1,610 | 1,480 | 1,168 | 0,877 | 0,773 |
| PVA/BA | 10 mg/L Methylene blue | 9,414 | 3,021 | 1,736 | 1,128 | 0,582 | 0,547 | 0,336 |
| | 5 mg/L Methylene blue | 4,913 | 4,536 | 2,487 | 0,829 | 0,438 | 0,295 | 0,247 |

Based on the obtained data, the dependence of the concentration on the sorption time and the type of adsorbent used is plotted (see Figure 19).

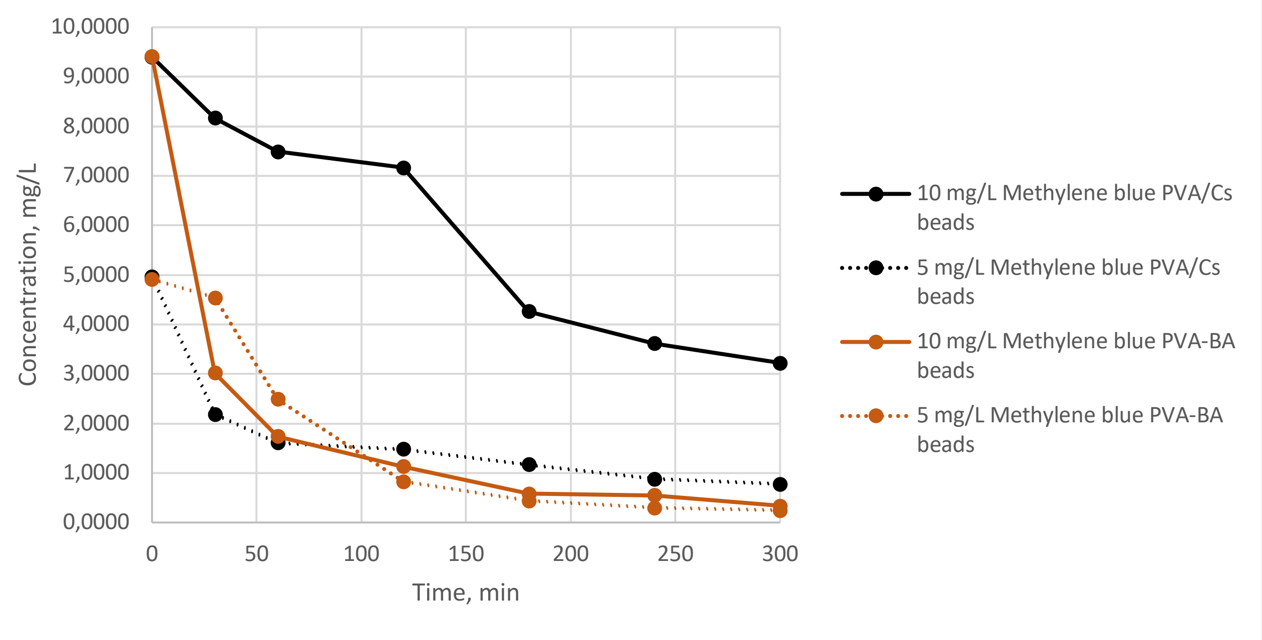


**Figure 19.** Dependence of Methylene blue concentration on sorption time and adsorbent

After analyzing the obtained results, it can be concluded that the additives used for the modification of the gel beads had a significant effect on the efficiency of Methylene blue sorption from water. The most efficient sorption of Methylene blue at all initial concentrations was achieved using gel beads of polyvinyl alcohol with boric acid. The lowest recorded concentration of Methylene blue after sorption was 0.247 mg/L. A final concentration of 0.336 mg/L was also reached by a 10 mg/L Methylene blue solution with PVA/BA gel beads. After the sorption experiment with PVA/BA gel beads, the Methylene blue concentration decreased by about 95%. Similar results were obtained with PVA/CS gel beads. The concentration of Methylene blue decreased by about 75%.

Based on the results obtained in this section, the sorption capacity of the adsorbents is further calculated.

### 3.3.1. Determination of sorption capacity

Lightweight and Freundlich adsorption equilibrium models are used to determine the sorption capacity presented in Section 2.3.1.

The dry mass of the gel beads is determined to form adsorption isotherm models (see Section 2.2, Equation 2.2.2.1). The calculated dry weight of the gel beads of polyvinyl alcohol with chitosan is 0.6312 g; the weight of the gel beads of polyvinyl alcohol with boric acid is 1.9702 g.

**Table 11.** Determination of Methylene blue sorption capacity of PVA/CS and PVA/BA gel beads

| | **Sorption capacity ($q_e$), mg/g** | |
|---|---|---|
| **Pollutant solution** | **PVA/CS gel beads** | **PVA/BA gel beads** |
| 10 mg/L Methylene blue | 2,608 | 1,164 |
| 5 mg/L Methylene blue | 1,700 | 0,611 |

Based on the data obtained, it can be concluded that the sorption capacity was best at an initial methylene blue concentration of 10 mg/L and most slowly at an initial contaminant concentration of 5 mg/L. Most likely, sorption occurred using PVA/CS gel beads (2.608 mg/g). The slowest adsorption occurred with PVA/BA gel beads (0.611 mg/g) when the initial methylene blue concentration was 5 mg/L. The highest sorption capacity was achieved using PVA/CS gel beads. Results are presented in Table 11.

### 3.3.2. Determination of sorption rate

Adsorption kinetics are described by pseudo 1st and pesudo 2nd order kinetic models. Pseudo 1st and pseudo 2nd order kinetic models and sorption rates are calculated based on the equations in Table 3 of Section 2.3.1.

The pseudo 1st and pesudo 2nd order sorption kinetic curves of polyvinyl alcohol gel beads are given below.

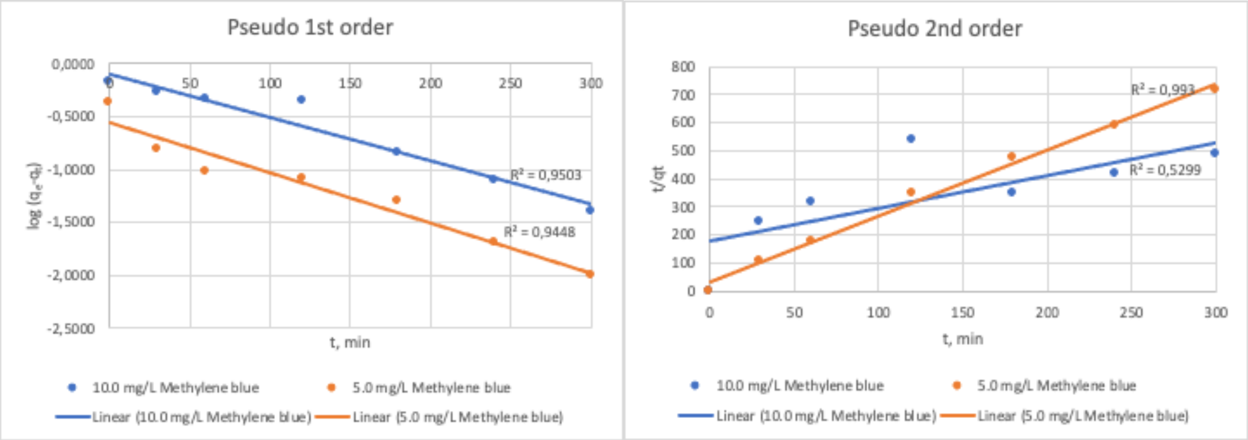


**Figure 20.** Pseudo 1st and pesudo 2nd order kinetic models of Polyvinyl alcohol with Chitosan gel beads

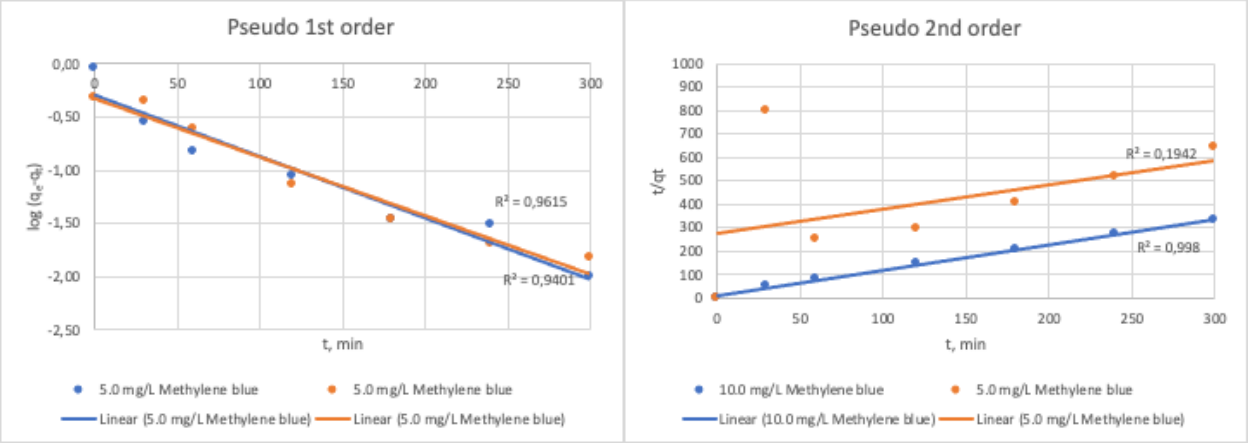


**Figure 21.** Pseudo 1st and pesudo 2nd order kinetic models of Polyvinyl alcohol with Boric acid gel beads

**Table 12.** Coefficients of pseudo 1st and pesudo 2nd order kinetic models

| **Parameters** | **Initial Methylene blue concentration 10 mg/L** | | | |
|---|---|---|---|---|
| | Pseudo 1st order | | Pseudo 2nd order | |
| | PVA/CS | PVA/BA | PVA/CS | PVA/BA |
| $R^2$ | 0,9503 | 0,9615 | 0,5299 | 0,1942 |
| L | -0,0940 | -0,3045 | 153,8343 | 9,8479 |
| S | -0,0041 | -0,0057 | 1,3777 | 1,0816 |
| $K_1/K_2$ | -0,0095 | -0,0132 | 0,0123 | 0,1188 |
| **Parameters** | **Initial Methylene blue concentration 5 mg/L** | | | |
| | Pseudo 1st order | | Pseudo 2nd order | |
| | PVA/CS | PVA/BA | PVA/CS | PVA/BA |
| $R^2$ | 0,9448 | 0,9401 | 0,9930 | 0,9980 |
| L | -0,5604 | -0,3233 | 37,9400 | 172,7392 |
| S | -0,0047 | -0,0055 | 2,3003 | 1,8824 |
| $K_1/K_2$ | -0,0109 | -0,0127 | 0,1395 | 0,0205 |

To determine the pseudo-first or pseudo-second-degree kinetic model describing the investigated sorption mechanism and calculate the sorption rate, the values of the coefficients $R^2$, S, L $K_1$, and $K_2$ are calculated according to the equations described in the research methodology (see Section 2.3.1, Table 6). The results are shown in Table 12.

For all adsorbents, the coefficient of determination ($R^2$) value is higher using the pseudo-degree II kinetics model, so this model is used to determine the reaction rates. From the adsorption kinetics coefficients $K_1$ and $K_2$, the adsorption rates h are calculated.

They depended on the concentration of the pollutant and the type of adsorbent used. The results are shown in the Table 13.

**Table 13.** Adsorption reaction rates depending on the sorbent and pollutant concentration used

| Type of gel beads | Micropollutants | Reaction rate (h), mg/g · min |
|---|---|---|
| PVA/CS | 10 mg/L Methylene blue | 0,0065 |
| | 5 mg/L Methylene blue | 0,0264 |
| PVA/BA | 10 mg/L Methylene blue | 0,1015 |
| | 5 mg/L Methylene blue | 0,0058 |

## 3.4. Results of the study of sorption properties of PVA gel beads with Tetracycline

To prepare the calibration curve, prepare solutions of different concentrations of Tetracycline by the dilution method and measure light absorption at 357 nm (Table 14).

**Table 14.** Concentration dependence of adsorption of Tetracycline solution

| Concentration, mg/L | Absorbtion |
|---|---|
| 1,0 | 0,034 |
| 2,0 | 0,069 |
| 3,0 | 0,104 |
| 4,0 | 0,136 |
| 5,0 | 0,171 |
| 7,5 | 0,257 |
| 10,0 | 0,349 |

From the known concentrations of the solution, a calibration graph (Figure 22) is drawn, from which the unknown concentrations will be determined later.

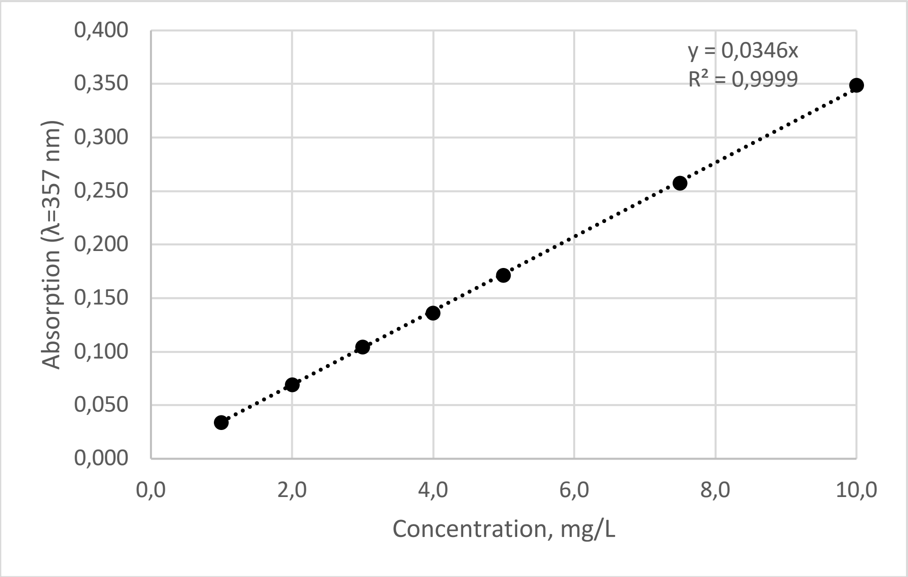


**Figure 22.** Concentration dependence of adsorption of Tetracycline solution

Stock solutions of Tetracycline were used for the sorption properties: 10 mg/L; 7.5 mg/L; 5 mg/L; 4 mg/L, 3 mg/L, 2 mg/L, 1 mg/L. Polyvinyl alcohol gel beads with boric acid and polyvinyl alcohol gel beads with chitosan are used as adsorbents in the study.

The light adsorption of Tetracycline solution of polyvinyl alcohol gel beads at 357 nm is measured. Initial Tetracycline concentrations are 5 mg/L and 1 mg/L. Sorption is performed for 180 min, samples are measured at 30, 60, 120, 180, 240, and 300 min. interval. 250 ml of each concentration solution and 10 g of dried gel beads of each type are used for the experiment. The variation of Tetracycline concentration with time and the adsorbent used is shown in Table 15. The concentration was calculated from the calibration curve (Figure 22).

**Table 15.** Dependence of Tetracycline concentration on sorption time and adsorbent

| Gel beads | Pollutant solution | 0 min | 30 min | 60 min | 120 min | 180 min | 240 min | 300 min |
|---|---|---|---|---|---|---|---|---|
| PVA/CS | 5 mg/L Tetracycline | 4,884 | 3,092 | 2,861 | 2,601 | 2,399 | 2,312 | 2,254 |
| | 1 mg/L Tetracycline | 0,954 | 0,838 | 0,578 | 0,462 | 0,405 | 0,318 | 0,260 |
| PVA/BA | 5 mg/L Tetracycline | 4,480 | 2,370 | 2,370 | 2,312 | 2,052 | 1,908 | 1,618 |
| | 1 mg/L Tetracycline | 1,040 | 1,012 | 0,954 | 0,954 | 0,983 | 0,925 | 0,896 |

Based on the obtained data, the dependence of the concentration on the sorption time and the type of adsorbent used is plotted (see Figure 23).

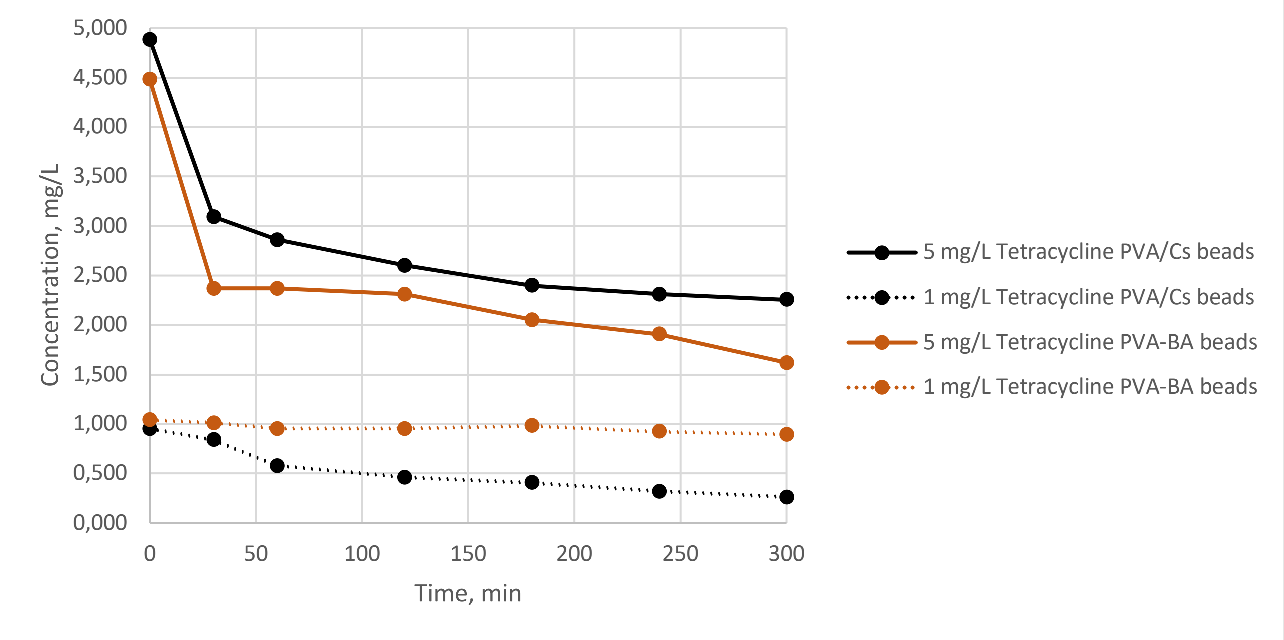


**Figure 23.** Dependence of Tetracycline concentration on sorption time and adsorbent

After analyzing the obtained results, it can be concluded that the additives used for the modification of the gel beads had an effect on the efficiency of Tetracycline sorption from water. The most efficient sorption of Tetracycline at all initial concentrations was achieved using gel beads of polyvinyl alcohol with chitosan. The lowest recorded concentration of Tetracycline after sorption was 0.260 mg/L. A final concentration of 2.254 mg/L was also reached by a 5 mg/L Tetracycline solution with PVA/BA gel beads. After the sorption experiment with PVA/BA gel beads, the Tetracycline concentration decreased by about 38.9 %. Better results were obtained with PVA/CS gel beads. The concentration of Tetracycline decreased by about 63.3 %.

Based on the results obtained in this section, the sorption capacity of the adsorbents is further calculated.

### 3.4.1. Determination of sorption capacity

Lightweight and Freundlich adsorption equilibrium models are used to determine the sorption capacity presented in Section 2.3.1.

The dry mass of the gel beads is determined to form adsorption isotherm models (see Section 2.2, Equation 1). The calculated dry weight of the gel beads of polyvinyl alcohol with chitosan is 0.6312 g; the weight of the gel beads of polyvinyl alcohol with boric acid is 1.9702 g.

**Table 16.** Determination of Tetracycline sorption capacity of PVA/CS and PVA/BA gel beads

| | **Sorption capacity ($q_e$), mg/g** | |
|---|---|---|
| **Pollutant solution** | **PVA/CS gel beads** | **PVA/BA gel beads** |
| 5 mg/L Tetracycline | 1,397 | 0,374 |
| 1 mg/L Tetracycline | 0,286 | 0,015 |

Based on the data obtained, it can be concluded that the sorption capacity was best at an initial Tetracycline concentration of 5 mg/L and most slowly at an initial contaminant concentration of 1 mg/L. Most likely, sorption occurred using PVA/CS gel beads (1,397 mg/g). The slowest adsorption occurred with PVA/BA gel beads (0,0115 mg/g) when the initial Tetracycline concentration was 1 mg/L. The highest sorption capacity was achieved using PVA/CS gel beads. Results are presented in Table 16.

### 3.4.2. Determination of sorption rate

Adsorption kinetics are described by pseudo 1st and pesudo 2nd order kinetic models. Pseudo 1st and pseudo 2nd order kinetic models and sorption rates are calculated based on the equations in Table 3 of Section 2.3.1.

The pseudo 1st and pesudo 2nd order sorption kinetic curves of polyvinyl alcohol gel beads are given below.

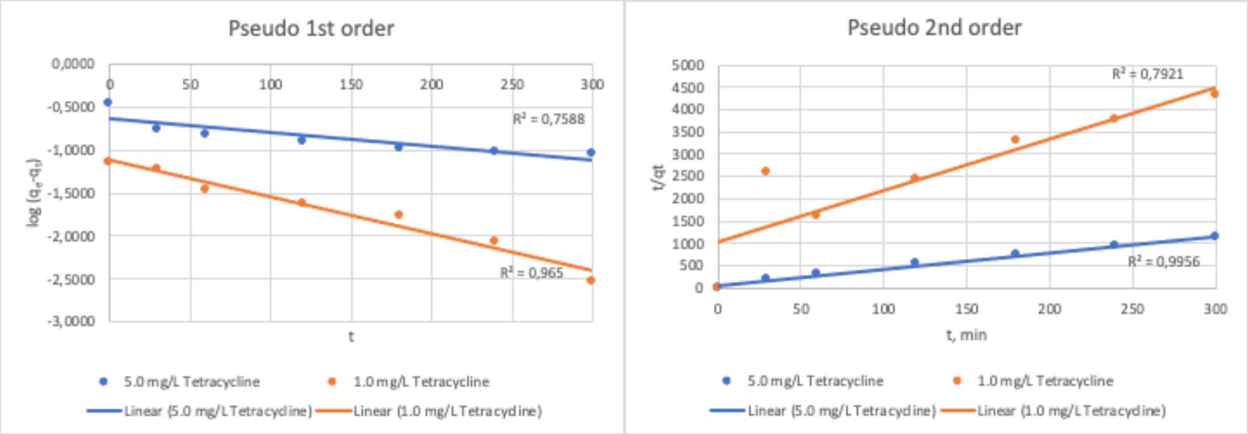


**Figure 24.** Pseudo 1st and pesudo 2nd order kinetic models of Polyvinyl alcohol with Chitosan gel beads

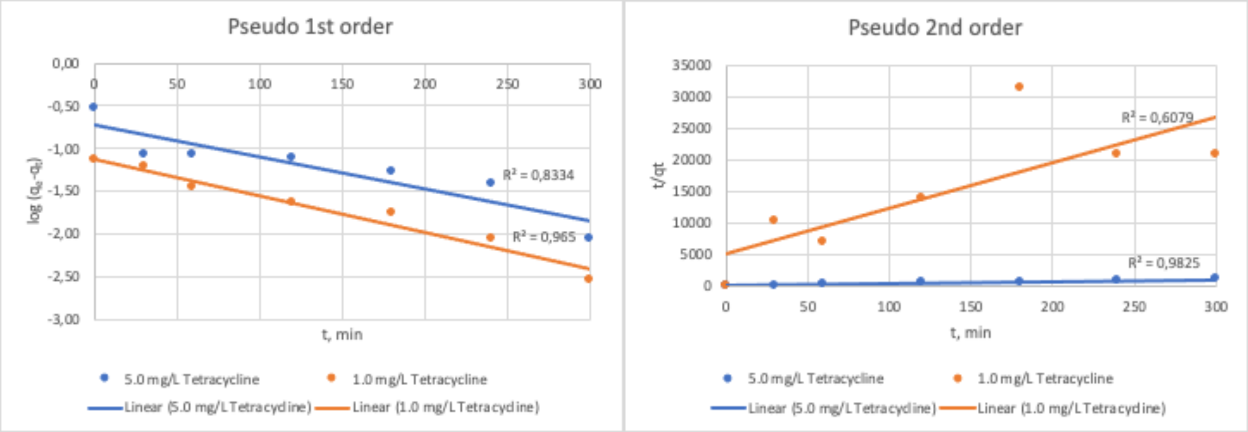


**Figure 25.** Pseudo 1st and pesudo 2nd order kinetic models of Polyvinyl alcohol with Boric acid gel beads

**Table 17.** Coefficients of pseudo 1st and pesudo 2nd order kinetic models

| **Parameters** | **Initial Tetracycline concentration 5 mg/L** | | | |
|---|---|---|---|---|
| | Pseudo 1st order | | Pseudo 2nd order | |
| | PVA/CS | PVA/BA | PVA/CS | PVA/BA |
| $R^2$ | 0,7588 | 0,8334 | 0,7921 | 0,6079 |
| L | -0,6432 | -0,7225 | 165,5705 | 83,7116 |
| S | -0,0016 | -0,0038 | 2,7541 | 3,3352 |
| K1/K2 | -0,0037 | -0,0087 | 0,0458 | 0,1329 |
| **Parameters** | **Initial Tetracycline concentration 1 mg/L** | | | |
| | Pseudo 1st order | | Pseudo 2nd order | |
| | PVA/CS | PVA/BA | PVA/CS | PVA/BA |
| $R^2$ | 0,9650 | 0,9650 | 0,9956 | 0,9825 |
| L | -1,1164 | -2,1168 | 856,5206 | 3967,7233 |
| S | -0,0043 | -0,0019 | 13,0364 | 82,5625 |
| K1/K2 | -0,0099 | -0,0043 | 0,1984 | 1,7180 |

To determine the pseudo-first or pseudo-second-degree kinetic model describing the investigated sorption mechanism and calculate the sorption rate, the values of the coefficients $R^2$, S, L $K_1$, and $K_2$ are calculated according to the equations described in the research methodology (see Section 2.3.1, Table 6). The results are shown in Table 17.

For all adsorbents, the coefficient of determination ($R^2$) value is higher using the pseudo-degree II kinetics model, so this model is used to determine the reaction rates. From the adsorption kinetics coefficients $K_1$ and $K_2$, the adsorption rates h are calculated.

Adsorption rates depended on the concentration of the pollutant and the type of adsorbent used. The results are shown in the Table 18.

**Table 18.** Adsorption reaction rates depending on the sorbent and pollutant concentration used

| Type of gel beads | Micropollutants | Reaction rate (h), mg/g · min |
|---|---|---|
| PVA/CS | 5 mg/L Tetracycline | 0,0060 |
| | 1 mg/L Tetracycline | 0,0012 |
| PVA/BA | 5 mg/L Tetracycline | 0,0119 |
| | 1 mg/L Tetracycline | 0,0003 |

### 3.5. Results of the study of sorption properties of PVA gel beads with Sulfamethoxazole

To prepare the calibration curve, prepare solutions of different concentrations of Sulfamethoxazole by the dilution method and measure light absorption at 258 nm (Table 19).

**Table 19.** Concentration dependence of adsorption of Sulfamethoxazole solution

| Concentration, mg/L | Absorbtion |
|---|---|
| 1,0 | 0,068 |
| 2,0 | 0,135 |
| 3,0 | 0,202 |
| 4,0 | 0,269 |
| 5,0 | 0,329 |
| 7,5 | 0,503 |
| 10,0 | 0,665 |

From the known concentrations of the solution, a calibration graph (Figure 26) is drawn, from which the unknown concentrations will be determined later.

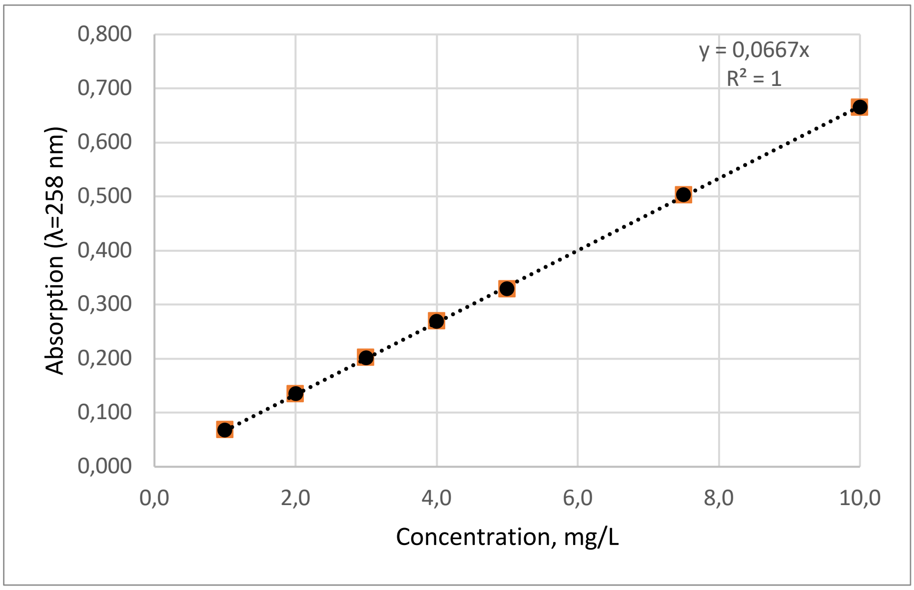


**Figure 26.** Concentration dependence of adsorption of Sulfamethoxazole solution

Stock solutions of Sulfamethoxazole were used for the sorption properties: 10 mg/L; 7.5 mg/L; 5 mg/L; 4 mg/L, 3 mg/L, 2 mg/L, 1 mg/L. Polyvinyl alcohol gel beads with boric acid and polyvinyl alcohol gel beads with chitosan are used as adsorbents in the study.

The light adsorption of Sulfamethoxazole solution of polyvinyl alcohol gel beads at 258 nm is measured. Initial Sulfamethoxazole concentrations are 5 mg/L and 1 mg/L. Sorption is performed for 180 min, samples are measured at 30, 60, 120, 180, 240, and 300 min. interval. 250 ml of each concentration solution and 10 g of dried gel beads of each type are used for the experiment. The variation of Sulfamethoxazole concentration with time and the adsorbent used is shown in Table 20. The concentration was calculated from the calibration curve (Figure 26).

**Table 20.** Dependence of Sulfamethoxazole concentration on sorption time and adsorbent

| Gel beads | Pollutant solution | 0 min | 30 min | 60 min | 120 min | 180 min | 240 min | 300 min |
|---|---|---|---|---|---|---|---|---|
| PVA/CS | 5 mg/L Sulfomethoxazole | 4,978 | 4,948 | 4,918 | 4,903 | 4,873 | 4,798 | 4,603 |
| | 1 mg/L Sulfomethoxazole | 1,109 | 1,034 | 1,034 | 1,019 | 0,975 | 0,945 | 0,900 |
| PVA/BA | 5 mg/L Sulfomethoxazole | 5,067 | 4,978 | 4,798 | 4,753 | 4,723 | 4,573 | 4,153 |
| | 1 mg/L Sulfomethoxazole | 1,004 | 0,975 | 0,900 | 0,885 | 0,900 | 0,840 | 0,810 |

Based on the obtained data, the dependence of the concentration on the sorption time and the type of adsorbent used is plotted (see Figure 27).

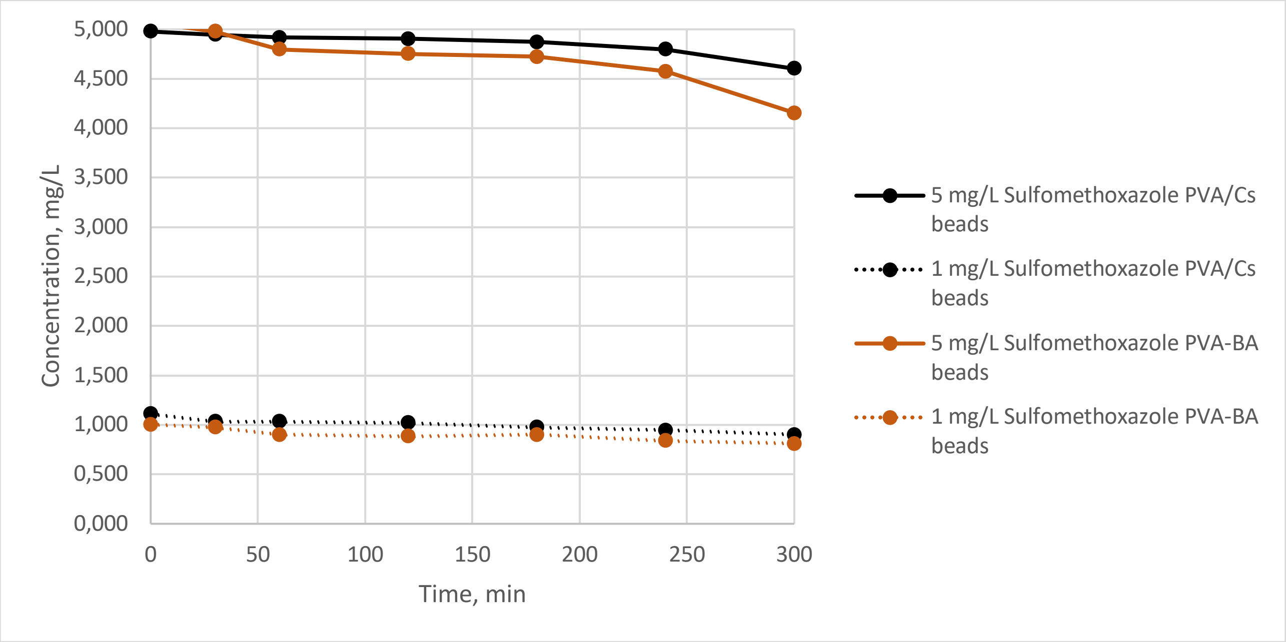


**Figure 27.** Dependence of Sulfamethoxazole concentration on sorption time and adsorbent

After analyzing the obtained results, it can be concluded that the additives used for the modification of the gel beads had an effect on the efficiency of Sulfamethoxazole sorption from water. The most efficient sorption of Sulfamethoxazole at all initial concentrations was achieved using gel beads of polyvinyl alcohol with boric acid. The lowest recorded concentration of Sulfamethoxazole after sorption was 0,810 mg/L. A final concentration of 4,152 mg/L was also reached by a 5 mg/L Sulfamethoxazole solution with PVA/BA gel beads. After the sorption experiment with PVA/BA gel beads, the Sulfamethoxazole concentration decreased by about 18,7 %. Better results were obtained with PVA/CS gel beads. The concentration of Sulfamethoxazole decreased by about 13,2 %.

Based on the results obtained in this section, the sorption capacity of the adsorbents is further calculated.

### 3.5.1. Determination of sorption capacity

Lightweight and Freundlich adsorption equilibrium models are used to determine the sorption capacity presented in Section 2.3.1.

The dry mass of the gel beads is determined to form adsorption isotherm models (see Section 2.2, Equation 1). The calculated dry weight of the gel beads of polyvinyl alcohol with chitosan is 0.6312 g; the weight of the gel beads of polyvinyl alcohol with boric acid is 1.9702 g.

**Table 21.** Determination of Sulfamethoxazole sorption capacity of PVA/CS and PVA/BA gel beads

| | **Sorption capacity ($q_e$), mg/g** | |
|---|---|---|
| **Pollutant solution** | **PVA/CS gel beads** | **PVA/BA gel beads** |
| 5 mg/L Sulfamethoxazole | 0,249 | 0,169 |
| 1 mg/L Sulfamethoxazole | 0,119 | 0,032 |

Based on the data obtained, it can be concluded that the sorption capacity was best at an initial Sulfamethoxazole concentration of 5 mg/L and most slowly at an initial contaminant concentration of 1 mg/L. Most likely, sorption occurred using PVA/BA gel beads (0,249 mg/g). The slowest adsorption occurred with PVA/CS gel beads (0,032 mg/g) when the initial Sulfamethoxazole concentration was 1 mg/L. The highest sorption capacity was achieved using PVA/BA gel beads. Results are presented in Table 21.

### 3.5.2. Determination of sorption rate

Adsorption kinetics are described by pseudo 1st and pesudo 2nd order kinetic models. Pseudo 1st and pseudo 2nd order kinetic models and sorption rates are calculated based on the equations in Table 3 of Section 2.3.1.

The pseudo 1st and pesudo 2nd order sorption kinetic curves of polyvinyl alcohol gel beads are given below.

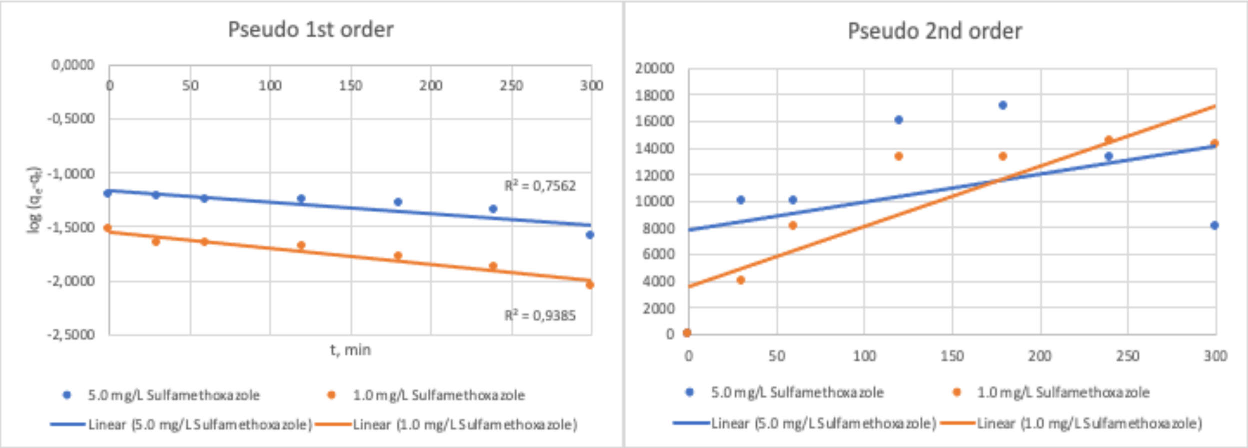


**Figure 28.** Pseudo 1st and pesudo 2nd order kinetic models of Polyvinyl alcohol with Chitosan gel beads

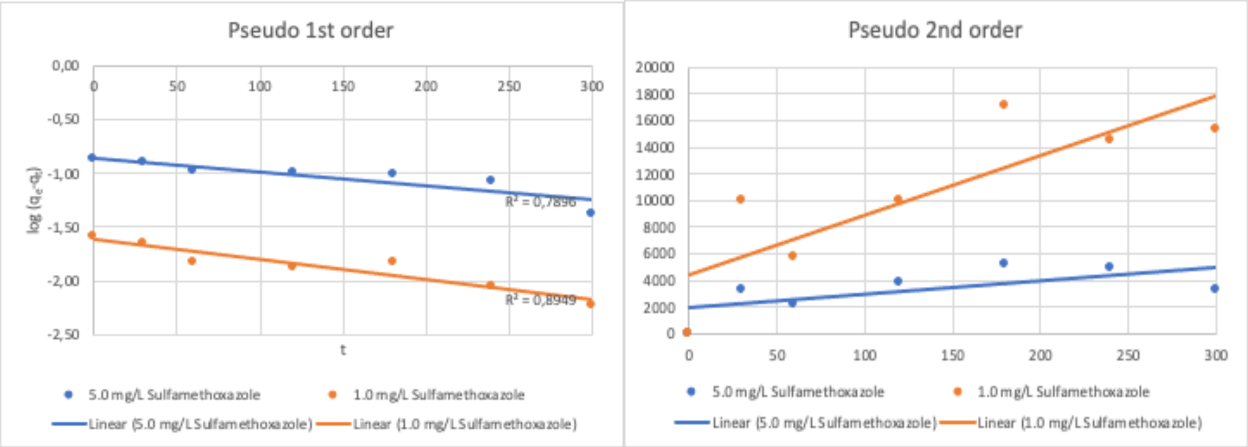


**Figure 29.** Pseudo 1st and pesudo 2nd order kinetic models of Polyvinyl alcohol with Boric acid gel beads

**Table 22.** Coefficients of pseudo 1st and pesudo 2nd order kinetic models

| **Parameters** | **Initial Sulfamethoxazole concentration 5 mg/L** | | | |
|---|---|---|---|---|
| | Pseudo 1st order | | Pseudo 2nd order | |
| | PVA/CS | PVA/BA | PVA/CS | PVA/BA |
| $R^2$ | 0,7562 | 0.7896 | 0.1729 | 0.4171 |
| L | -1.1670 | -0.8527 | 7802.5341 | 1905.5373 |
| S | -0.0010 | -0.0013 | 21.3932 | 10.0884 |
| K1/K2 | -0.0024 | -0.0031 | 0.0587 | 0.0534 |
| **Parameters** | **Initial Sulfamethoxazole concentration 1 mg/L** | | | |
| | Pseudo 1st order | | Pseudo 2nd order | |
| | PVA/CS | PVA/BA | PVA/CS | PVA/BA |
| $R^2$ | 0.9385 | 0.8949 | 0.7699 | 0.6894 |
| L | -1.5433 | -1.6170 | 3632.9489 | 4467.4432 |
| S | -0.0015 | -0.0018 | 45.2698 | 44.6790 |
| K1/K2 | -0.0034 | -0.0042 | 0.5641 | 0.4468 |

To determine the pseudo-first or pseudo-second-degree kinetic model describing the investigated sorption mechanism and calculate the sorption rate, the values of the coefficients $R^2$, S, L $K_1$, and $K_2$ are calculated according to the equations described in the research methodology (see Section 2.3.1, Table 6). The results are shown in Table 22.

For all adsorbents, the coefficient of determination ($R^2$) value is higher using the pseudo-degree II kinetics model, so this model is used to determine the reaction rates. From the adsorption kinetics coefficients $K_1$ and $K_2$, the adsorption rates h are calculated.

Adsorption rates depended on the concentration of the pollutant and the type of adsorbent used. The results are shown in the Table 23.

**Table 23.** Adsorption reaction rates depending on the sorbent and pollutant concentration used

| Type of gel beads | Micropollutants | Reaction rate (h), mg/g · min |
|---|---|---|
| PVA/CS | 5 mg/L Sulfamethoxazole | 0.0060 |
| | 1 mg/L Sulfamethoxazole | 0.0012 |
| PVA/BA | 5 mg/L Sulfamethoxazole | 0.0119 |
| | 1 mg/L Sulfamethoxazole | 0.0003 |

### 3.6. Biological synthetic wastewater treatment with active sludge and PVA gel beads

After performing the PVA/CS and PVA/BA gel beads sorption studies and verifying their effectiveness, the studies were transferred to a biological reactor. This study helped to find out how the granules perform the treatment of synthetic wastewater. The study was carried out in five different reactors with different gel beads and activated sludge.

After the gel beads were transferred to the reactor, their mechanical properties and strength could be ascertained again. PVA/BA granules do not decompose practically during the whole period. PVA/BA granules also had good mechanical properties in a reactor with activated sludge. No mechanical damage could be seen. However, another type of granule (PVA/CS) showed less good mechanical properties and strength. PVA/CS beads were visibly damaged after seven days, and small fragments of beads could be seen in the synthetic effluent solution. The PVA/CS gel beads that were placed in the reactor with activated sludge decompose entirely. Due to its poor mechanical properties, it could not withstand friction and crumble.

Contaminants (phosphate, nitrate, ammonia, total nitrogen, total phosphorus, total organic carbon) were measured during the PVA/CS and PVA/BA gel beads studies in the reactor. The results obtained are shown in Table 24. During the study, a decrease in pollutants (phosphate, nitrate, ammonia, total nitrogen, total phosphorus) was observed due to biological wastewater treatment. However, total organic carbon concentrations have increased. This was caused by glucose being supplemented every day as a carbon source for microorganisms living in the sludge.

**Table 24.** Results of biological synthetic wastewater treatment with active sludge and PVA gel beads.

| | **Total Nitrogen** | **Total Phosphorus** | **Phosphate** | **Nitrate** | **Ammonia** | **Total organic carbon** |
|---|---|---|---|---|---|---|
| 05-04 Active Sludge | 28.0 | 55.0 | 115.2 | - | 60.9 | 21.3 |
| 05-05 Active Sludge | 29.0 | 53.5 | 95.6 | 9.6 | 34.5 | 35.2 |
| 05-05 PVA/CS gel beads+Active Sludge | 64.0 | 57.0 | 105.2 | 124.4 | 13.7 | 23.3 |
| 05-05 PVA/BA gel beads+Active Sludge | 24.0 | 46.0 | 76.4 | 147.6 | 0.1 | 410.1 |
| 05-05 PVA/CS gel beads | 25.0 | 56.5 | 118.0 | 0.0 | 58.7 | 395.4 |
| 05-05 PVA/BA gel beads | 23.0 | 16.0 | 34.8 | 0.0 | 41.2 | 56.6 |
| 05-07 Active Sludge | 31.0 | 0.0 | 102.0 | 12.8 | 33.4 | 50.4 |
| 05-07 PVA/CS gel beads+Active Sludge | 28.0 | 47.5 | 104.4 | 26.0 | 11.5 | 134.2 |
| 05-07 PVA/BA gel beads+Active Sludge | 28.0 | 27.5 | 63.6 | 178.8 | 0.3 | 124.4 |
| 05-07 PVA/CS gel beads | 26.0 | 41.5 | 124.5 | 0.0 | 58.5 | 505.3 |
| 05-07 PVA/BA gel beads | 26.0 | 20.5 | 29.2 | 0.0 | 53.2 | 215.1 |
| 05-10 Active Sludge | 3.0 | 51.0 | 103.2 | 0.0 | 61.0 | 37.4 |
| 05-10 PVA/CS gel beads+Active sludge | 5.0 | 24.0 | 145.0 | 63.0 | 128.8 | 120.8 |
| 05-10 PVA/BA gel beads+Active Sludge | 3.0 | 7.0 | 43.0 | 0.0 | 5.1 | 121.0 |
| 05-10 PVA/CS gel beads | 1.0 | 22.0 | 124.0 | 0.0 | 37.2 | 1129.0 |
| 05-10 PVA/BA gel beads | 0.0 | 2.0 | 32.0 | 0.0 | 35.6 | 191.6 |

To evaluate the efficiency of pollutants treatment in synthetic wastewater using PVA/CS and PVA/BA gel beads, it is necessary to compare different reactor fillers' impacts for wastewater treatment. In the Table 25 is the results of Contaminant removal efficiency in biological treatment of synthetic wastewater with activated sludge and PVA gel granules. PVA/BA gel beads had the best pollutants removal efficiency. PVA/BA gel beads also demonstrated excellent results with active sludge. PVA/CS gel beads did not show good cleaning efficiency, but this may be closely related to their poor mechanical properties and degradation during the study.

A value with a minus sign indicates that the concentration has not decreased over time but has increased. Such results are observed in the TOC parameters, as the sludge was fed daily with glucose and synthetic effluent.

**Table 25.** Contaminant removal efficiency in biological treatment of synthetic wastewater with activated sludge and PVA gel granules.

| | **TN removal efficiency, %** | **TP Removal efficiency, %** | **TOC Removal efficiency, %** | **$NO^{3-}$ Removal efficiency, %** | **$PO_4^{3-}$ Removal efficiency, %** | **$NH_3$ Removal efficiency, %** |
|---|---|---|---|---|---|---|
| Active Sludge | 89.3 | 7.3 | -75.6 | 100 | 10.4 | 1.2 |
| PVA/CS gel beads+Active Sludge | 82.1 | 56.4 | -467.1 | 49.4 | -25.9 | -111.5 |
| PVA/BA gel beads+Active Sludge | 89.3 | 87.3 | -468.1 | 100.0 | 62.7 | 91.6 |
| PVA/CS gel beads | 96.4 | 60.0 | -5200.5 | 0.0 | -7.6 | 38.9 |
| PVA/BA gel beads | 97.1 | 96.4 | -799.5 | 0.0 | 72.2 | 41.5 |

## Conclusions

1. A literature review has shown that biological wastewater treatment using carrier material is promising and easily adapted to existing wastewater treatment plants. Carriers have properties that allow microorganisms involved in the biological process of wastewater treatment to be immobilized inside them. One innovative, environmentally friendly technology is the adsorption of water pollutants with gel beads made from polymer polyvinyl alcohol.
2. The most suitable synthesis conditions for the production of polyvinyl alcohol gel beads: (1) PVA/CS – dissolve PVA in DI $H_2O$ at 80°C for 5h | cross-linking agent: 0.3M NaOH; (2) PVA/BA - dissolve PVA in DI $H_2O$ at 23°C for 1h and 55°C for 5h | cross-linking agent: saturated $H_3BO_3$ solution with 1% $CaCl_2$. The synthesis of the two types of hydrogels also revealed their mechanical properties. PVA/CS has poor chemical and mechanical resistance, and PVA/BA has strong stability for long-term use.
3. Sorption studies showed that the additives used for gel beads influenced the sorption efficiency. Methylene blue, sulfamethoxazole, and tetracycline were used to study the sorption properties of polyvinyl alcohol gel beads. Initial concentrations of contaminants are 10 mg/L, 5 mg/L, 1 mg/L. The sorption experiment was observed for 300 minutes. The best sorption capacity of 10 mg/L methylene blue solution was determined for PVA/BA – 2.608 mg/g, which is 2.24 times higher than PVA/CS. The highest sorption capacity with tetracycline was PVA/CS 1.397 mg/g, and it was 3.73 times higher than PVA/BA. Polyvinyl alcohol gel beads with chitosan additive also showed better sorption results than PVA/BA. It was 0.249 mg/g, while the sorption capacity of PVA/BA was 0.169 (1.47 lower).
4. Synthetic wastewater treatment studies in the biological reactor showed that both PVA/BA gel beads and PVA/BA gel beads with activated sludge had better removal efficiency. The PVA/BA gel beads reached a 97.1 % total nitrogen removal efficiency. Compared with the total nitrogen removal efficiency of PVA/BA gel beads with active sludge (89.3 %), it is 1.09 times higher. The PVA/BA gel beads also have better total phosphorus, nitrates, phosphates snd ammonia removal efficiency than PVA/BA gel beads with active sludge.

## List of references

1. SIYAL, A.A., SHAMSUDDIN, M.R., LOW, A. and RABAT, N.E. *A Review on Recent Developments in the Adsorption of Surfactants from Wastewater.*, 2020 Available from: http://www.sciencedirect.com/science/article/pii/S0301479719315154 ISBN 0301-4797. DOI https://doi.org/10.1016/j.jenvman.2019.109797.
2. SINHA, V. and CHAKMA, S. *Advances in the Preparation of Hydrogel for Wastewater Treatment: A Concise Review.* , 2019 Available from: http://www.sciencedirect.com/science/article/pii/S221334371930418X ISBN 2213-3437. DOI https://doi.org/10.1016/j.jece.2019.103295.
3. WANG, J., et al. Granule-Based Immobilization and Activity Enhancement of Anammox Biomass Via PVA/CS and PVA/CS/Fe Gel Beads. *Bioresource Technology*, 2020, vol. 309. pp. 123448. Available. from: https://www.sciencedirect.com/science/article/pii/S0960852420307203 ISSN 0960-8524. DOI https://doi.org/10.1016/j.biortech.2020.123448.
4. Sun, L., Wang, J., Liang, J. *et al.* Boric Acid Cross-linked 3D Polyvinyl Alcohol Gel Beads by NaOH-Titration Method as a Suitable Biomass Immobilization Matrix. *J Polym Environ***28,** 532–541 (2020). https://doi.org/10.1007/s10924-019-01610-z
5. Li Jin, Renbi Bai. Mechanisms of Lead Adsorption on Chitosan/PVA Hydrogel Beads.Langmuir 2002 18 (25), 9765-9770. *Langmuir* 2002, 18, 25, 9765–9770. Publication Date:October 30, 2002. https://doi.org/10.1021/la025917l
6. ZHAO, Y., et al. Insights into Biofilm Carriers for Biological Wastewater Treatment Processes: Current State-of-the-Art, Challenges, and Opportunities. , 2019 Available from: http://www.sciencedirect.com/science/article/pii/S0960852419308491 ISBN 0960-8524. DOI https://doi.org/10.1016/j.biortech.2019.121619.
7. AN, Y., et al. *Enhancing Biodegradability of Industrial Park Wastewater by Packing Carriers and Limited Aeration in the Hydrolysis Process.* , 2020 Available from: http://www.sciencedirect.com/science/article/pii/S0959652620316851 ISBN 0959-6526. DOI https://doi.org/10.1016/j.jclepro.2020.121638.
8. EL-SHAFAI, S.A. and ZAHID, W.M. Performance of Aerated Submerged Biofilm Reactor Packed with Local Scoria for Carbon and Nitrogen Removal from Municipal Wastewater. , 2013 Available from: http://www.sciencedirect.com/science/article/pii/S0960852413009462 ISBN 0960-8524. DOI https://doi.org/10.1016/j.biortech.2013.06.027.
9. ZHANG, X., et al. *A Sustainable Bio-Carrier Medium for Wastewater Treatment: Modified Basalt Fiber.* , 2019 Available from: http://www.sciencedirect.com/science/article/pii/S0959652619310492 ISBN 0959-6526. DOI https://doi.org/10.1016/j.jclepro.2019.03.333.
10. DONG, Z., LU, M., HUANG, W. and XU, X. *Treatment of Oilfield Wastewater in Moving Bed Biofilm Reactors using a Novel Suspended Ceramic Biocarrier.* , 2011 Available from: http://www.sciencedirect.com/science/article/pii/S0304389411010995 ISBN 0304-3894. DOI https://doi.org/10.1016/j.jhazmat.2011.09.001.
11. DENG, L., et al. *New Functional Biocarriers for Enhancing the Performance of a Hybrid Moving Bed Biofilm Reactor–membrane Bioreactor System.* , 2016 Available from:

http://www.sciencedirect.com/science/article/pii/S0960852416301900 ISBN 0960-8524. DOI https://doi.org/10.1016/j.biortech.2016.02.057.

12. ZHANG, X., et al. Biofilm Characteristics in Natural Ventilation Trickling Filters (NVTFs) for Municipal Wastewater Treatment: Comparison of Three Kinds of Biofilm Carriers. , 2016 Available from: http://www.sciencedirect.com/science/article/pii/S1369703X15301078 ISBN 1369-703X. DOI https://doi.org/10.1016/j.bej.2015.11.009.
13. HUANG, T., XU, J. and CAI, D. Efficiency of Active Barriers Attaching Biofilm as Sediment Capping to Eliminate the Internal Nitrogen in Eutrophic Lake and Canal. , 2011 Available from: http://www.sciencedirect.com/science/article/pii/S100107421060469X ISBN 1001-0742. DOI https://doi.org/10.1016/S1001-0742(10)60469-X.
14. WENJIE, Z., et al. *PVA-Gel Beads Enhance Granule Formation in a UASB Reactor.* , 2008 Available from: http://www.sciencedirect.com/science/article/pii/S0960852408001788 ISBN 0960-8524. DOI https://doi.org/10.1016/j.biortech.2008.02.040.
15. YANG, X., et al. *Selection and Application of Agricultural Wastes as Solid Carbon Sources and Biofilm Carriers in MBR.* , 2015 Available from: http://www.sciencedirect.com/science/article/pii/S0304389414007742 ISBN 0304-3894. DOI https://doi.org/10.1016/j.jhazmat.2014.09.036.
16. DENG, L., et al. *New Functional Biocarriers for Enhancing the Performance of a Hybrid Moving Bed Biofilm Reactor–membrane Bioreactor System.* , 2016 Available from: http://www.sciencedirect.com/science/article/pii/S0960852416301900 ISBN 0960-8524. DOI https://doi.org/10.1016/j.biortech.2016.02.057.
17. FAKHRAEI GHAZVINI, M., VAHEDI, M., NAJAFI NOBAR, S. and SABOURI, F. Investigation of the MOF Adsorbents and the Gas Adsorptive Separation Mechanisms. Journal of Environmental Chemical Engineering, 2021, vol. 9, no. 1. pp. 104790. Available from: https://www.sciencedirect.com/science/article/pii/S2213343720311398 ISSN 2213-3437. DOI https://doi.org/10.1016/j.jece.2020.104790.
18. HOSSEINNIA, A., HASHTROUDI, M.S., PAZOUKI, M. and BANIFATEMI, M. Removal of Surfactants from Wastewater by Rice Husk. *Iranian Journal of Chemical Engineering*, 2006, vol. 3, no. 3. pp. 44-50.
19. CRINI, G. and BADOT, P. Application of Chitosan, a Natural Aminopolysaccharide, for Dye Removal from Aqueous Solutions by Adsorption Processes using Batch Studies: A Review of Recent Literature. , 2008 Available from: http://www.sciencedirect.com/science/article/pii/S0079670007001293 ISBN 0079-6700. DOI https://doi.org/10.1016/j.progpolymsci.2007.11.001.
20. DE GISI, S., LOFRANO, G., GRASSI, M. and NOTARNICOLA, M. An Overview of Low-Cost Adsorbents for Wastewater Treatment. *Sustainable Materials and Technologies*, 2015, vol. 9. pp. 10.
21. ZHANG, X., et al. Impact of COD/N on Anammox Granular Sludge with Different Biological Carriers. Science of the Total Environment, 2020, vol. 728. pp. 138557. Available from: *https://www.sciencedirect.com/science/article/pii/S0048969720320738ISSN 0048-9697.* DOI https://doi.org/10.1016/j.scitotenv.2020.138557.
22. UNNIKRISHNAN, P. and SRINIVAS, D. *Chapter 3 - Heterogeneous Catalysis.* JOSHI, Sunil S. and RANADE, Vivek V. eds., Amsterdam: Elsevier, 2016 Available from:

http://www.sciencedirect.com/science/article/pii/B9780128014578000033 ISBN 9780-128014578. DOI https://doi.org/10.1016/B978-0-12-801457-8.00003-3.

23. HODZIC, A. *12 - Re-use, Recycling and Degradation of Composites.* BAILLIE, Caroline ed., Woodhead Publishing, 2004 Available from: http://www.sciencedirect.com/science/article/pii/B9781855737396500154 ISBN 9781-855737396. DOI https://doi.org/10.1016/B978-1-85573-739-6.50015-4.
24. GOLNARAGHI GHOMI, A., ASASIAN-KOLUR, N., SHARIFIAN, S. and GOLNARAGHI, A. *Biosorpion for Sustainable Recovery of Precious Metals from Wastewater.* , 2020 Available from: http://www.sciencedirect.com/science/article/pii/S2213343720303444 ISBN 2213-3437. DOI https://doi.org/10.1016/j.jece.2020.103996.
25. BENI, A.A. and ESMAEILI, A. *Biosorption, an Efficient Method for Removing Heavy Metals from Industrial Effluents: A Review.* , 2020 Available from: http://www.sciencedirect.com/science/article/pii/S2352186418304346 ISBN 2352-1864. DOI https://doi.org/10.1016/j.eti.2019.100503.
26. FOMINA, M. and GADD, G.M. *Biosorption: Current Perspectives on Concept, Definition and Application.* , 2014 Available from: http://www.sciencedirect.com/science/article/pii/S0960852413019421 ISBN 0960-8524. DOI https://doi.org/10.1016/j.biortech.2013.12.102.
27. SURKATTI, R. and EL-NAAS, M.H. Biological Treatment of Wastewater Contaminated with P-Cresol using Pseudomonas Putida Immobilized in Polyvinyl Alcohol (PVA) Gel. , 2014 Available from: http://www.sciencedirect.com/science/article/pii/S2214714414000130 ISBN 2214-7144. DOI https://doi.org/10.1016/j.jwpe.2014.03.008.
28. WANG, Y., LIU, Y., FENG, M. and WANG, L. Study of the Treatment of Domestic Sewage using PVA Gel Beads as a Biomass Carrier. *Journal of Water Reuse and Desalination*, 2018, vol. 8, no. 3. pp. 340-349. DOI https://doi.org/10.2166/wrd.2017.181
29. ALI, M., et al. *Rapid and Successful Start-Up of Anammox Process by Immobilizing the Minimal Quantity of Biomass in PVA-SA Gel Beads.* , 2015 Available from: http://www.sciencedirect.com/science/article/pii/S0043135415002535 ISBN 0043-1354. DOI https://doi.org/10.1016/j.watres.2015.04.024.
30. MOHAMMADZADEH PAKDEL, P. and PEIGHAMBARDOUST, S.J. *A Review on Acrylic Based Hydrogels and their Applications in Wastewater Treatment.* , 2018 Available from: http://www.sciencedirect.com/science/article/pii/S0301479718303098 ISBN 0301-4797. DOI https://doi.org/10.1016/j.jenvman.2018.03.076.
31. WANG, J., LIANG, J., SUN, L. and GAO, S. *PVA/CS and PVA/CS/Fe Gel Beads' Synthesis Mechanism and their Performance in Cultivating Anaerobic Granular Sludge.* , 2019 Available from: http://www.sciencedirect.com/science/article/pii/S0045653518323361ISBN 0045-6535. DOI https://doi.org/10.1016/j.chemosphere.2018.12.014.
32. TUYEN, N.V., et al. *Nitrogen Removal Performance of Anammox Process with PVA–SA Gel Bead Crosslinked with Sodium Sulfate as a Biomass Carrier.* , 2018 Available from: http://www.sciencedirect.com/science/article/pii/S1226086X1830337X ISBN 1226-086X. DOI https://doi.org/10.1016/j.jiec.2018.07.004.
33. TAKEI, T., IKEDA, K., IJIMA, H. and KAWAKAMI, K. *Fabrication of Poly(Vinyl Alcohol) Hydrogel Beads Crosslinked using Sodium Sulfate for Microorganism Immobilization.* , 2011

Available from: http://www.sciencedirect.com/science/article/pii/S1359511310003946 ISBN 1359-5113. DOI https://doi.org/10.1016/j.procbio.2010.10.011.

34. HUI, B., ZHANG, Y. and YE, L. *Preparation of PVA Hydrogel Beads and Adsorption Mechanism for Advanced Phosphate Removal.* , 2014 Available from: http://www.sciencedirect.com/science/article/pii/S1385894713012163 ISBN 1385-8947. DOI https://doi.org/10.1016/j.cej.2013.09.045.
35. BAI, X., et al. *Preparation and Characterization of a Novel Macroporous Immobilized Micro-Organism Carrier.* , 2010 Available from: http://www.sciencedirect.com/science/article/pii/S1369703X1000015X ISBN 1369-703X. DOI https://doi.org/10.1016/j.bej.2010.01.004.
36. YU, Y., SHU, Y. and YE, L. In Situ Crosslinking of Poly (Vinyl Alcohol)/Graphene Oxide-Glutamic Acid Nano-Composite Hydrogel as Microbial Carrier: Intercalation Structure and its Wastewater Treatment Performance. , 2018 Available from: http://www.sciencedirect.com/science/article/pii/S1385894717321502 ISBN 1385-8947. DOI https://doi.org/10.1016/j.cej.2017.12.038.
37. XU, X., et al. *Nitrogen Removal and Microbial Diversity of Activated Sludge Entrapped in Modified Poly(Vinyl Alcohol)–sodium Alginate Gel.* , 2017 Available from: http://www.sciencedirect.com/science/article/pii/S096483051730759X ISBN 0964-8305. DOI https://doi.org/10.1016/j.ibiod.2017.07.014.
38. KIM, J., KANG, J., LEE, S. and KIM, S. Immobilization of Layered Double Hydroxide in Poly(Vinylidene Fluoride)/Poly(Vinyl Alcohol) Polymer Matrices to Synthesize Bead-Type Adsorbents for Phosphate Removal from Natural Water. , 2019 Available from: http://www.sciencedirect.com/science/article/pii/S0169131719300043 ISBN 0169-1317. DOI https://doi.org/10.1016/j.clay.2019.01.004.
39. XU, X., et al. Nitrogen Removal and Microbial Diversity of Activated Sludge Entrapped in Modified Poly(Vinyl Alcohol)–sodium Alginate Gel. , 2017 Available from: http://www.sciencedirect.com/science/article/pii/S096483051730759X ISBN 0964-8305. DOI https://doi.org/10.1016/j.ibiod.2017.07.014.
40. YU, Y., SHU, Y. and YE, L. In Situ Crosslinking of Poly (Vinyl Alcohol)/Graphene Oxide-Glutamic Acid Nano-Composite Hydrogel as Microbial Carrier: Intercalation Structure and its Wastewater Treatment Performance. , 2018 Available from: http://www.sciencedirect.com/science/article/pii/S1385894717321502 ISBN 1385-8947. DOI https://doi.org/10.1016/j.cej.2017.12.038.
41. BAI, X., et al. Preparation and Characterization of a Novel Macroporous Immobilized Micro-Organism Carrier. , 2010 Available from: http://www.sciencedirect.com/science/article/pii/S1369703X1000015X ISBN 1369-703X. DOI https://doi.org/10.1016/j.bej.2010.01.004.
42. RATHI, B.S. and KUMAR, P.S. Application of Adsorption Process for Effective Removal of Emerging Contaminants from Water and Wastewater. Environmental Pollution, 2021, vol. 280. pp. 116995. Available from: https://www.sciencedirect.com/science/article/pii/S0269749121005777 ISSN 0269-7491. DOI https://doi.org/10.1016/j.envpol.2021.116995.
43. ABROMAITIS, V., RACYS, V., VAN DER MAREL, P. and MEULEPAS, R.J.W. Biodegradation of Persistent Organics can Overcome Adsorption–desorption Hysteresis in

Biological Activated Carbon Systems. Chemosphere, 2016, vol. 149. pp. 183-189. Available from: https://www.sciencedirect.com/science/article/pii/S004565351630090X ISSN 0045-6535. DOI https://doi.org/10.1016/j.chemosphere.2016.01.085.