

Review on Recent Progress in Wastewater Treatments via Using Alginate-Based Gels as Adsorbent Materials

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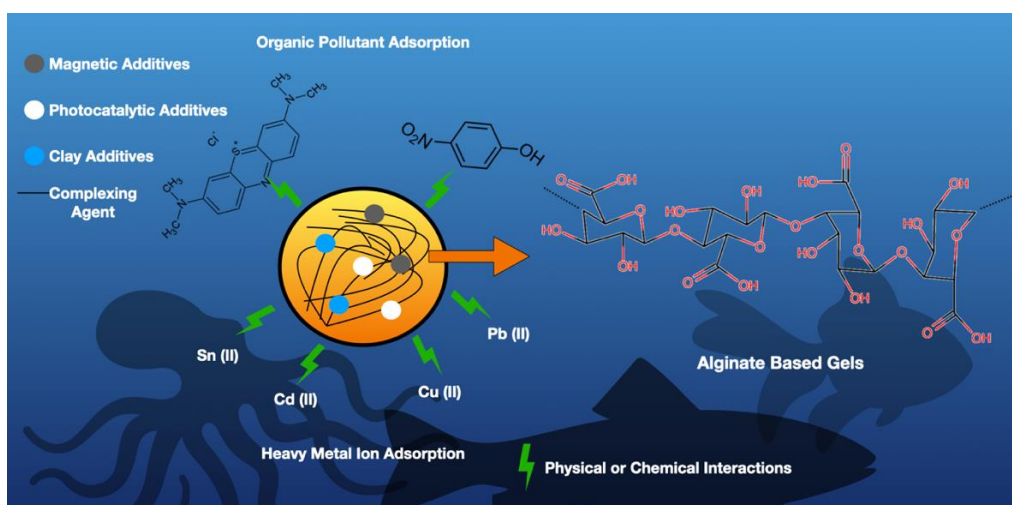
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Abstract

Wastewater constitutes a significant threat to human and environmental well-being owing to its high concentration of toxic compounds. The existence of heavy metal ions and organic pollutants in wastewater to an acceptable standard level is crucial. Adsorption, an economical, easily implementable, and eco-friendly method, is widely employed to eliminate targeted contaminants from wastewater. A wide array of adsorbent materials has been utilized throughout history, and novel functional materials continue to be developed. Biopolymers, characterized by their chemical structure, cost-effectiveness, environmental compatibility, biocompatibility, and biodegradability, have found applications in adsorption studies. Among these, alginate stands out due to its ability to form gels in the presence of divalent cations, facilitating the entrapment and removal of contaminants. Alginate, a biocompatible and biodegradable polysaccharide, is particularly utilized in adsorption processes due to its chemical properties. Alginate-based materials can form hydrogels, which provide a large surface area for adsorption and enhance the removal efficiency of heavy metals and organic pollutants. In addition to these advantages, alginate hydrogels may have low mechanical strength and, in some cases, may show undesirable dissolution tendencies. A variety of methodologies can be employed to eliminate weaknesses. This review delves into the use of alginate matrix gels for the removal of pollutants in wastewater, featuring an array of relevant studies. Moreover, a concise overview of the adsorption process, kinetics, and isotherms is provided.

Keywords

Adsorption, alginate gels, wastewater treatment



1. Introduction

With the advancement of technology, the growth of industrialization, and the rapid pace of urbanization, there has been a steady rise in the volume of wastewater generated daily. The pollutants present in wastewater pose substantial threats to both human health and the environment. Not only can these pollutants have toxic effects on the human body and lead to the development of cancer, but they also inflict severe damage on the natural surroundings. Consequently, it is imperative to effectively treat and purify the pollutants found in wastewater under specific standards. In addition to international organizations such as the World Health Organization (WHO), Food and Agriculture Organization (FAO), and European Union (EU), individual countries establish specific standards for water quality within their jurisdictions. FAO has provided guidelines on the acceptable levels of heavy metal ions in irrigation water, as outlined in Table 1. The presence of heavy metal ions in wastewater poses potential risks to both the ecosystem and human health. These heavy metals exhibit toxicity, and carcinogenic properties, and are non-biodegradable, thereby having the potential to contaminate water sources and jeopardize the well-being of individuals. Wastewater originating from various sectors including plating and electroplating, battery manufacturing, pesticide production, mining activities, tanning processes, textile manufacturing, metal smelting, petrochemical industries, paper production, and electrolysis applications is frequently found to contain significant concentrations of heavy metals [1]. Arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn) are among the heavy metals commonly detected in wastewater [2]. Besides the heavy metal ions, organic contaminants present in wastewater have the potential to pose significant hazards to both the environment and public health. This category of pollutants encompasses a wide range of chemicals, such as dyes, humic substances, phenolic compounds, petroleum derivatives, surfactants, pesticides, and pharmaceuticals [3].

Before discharging wastewater into the natural environment, it is crucial to ensure that the levels of pollutants, including metal ions and organic contaminants, are reduced to below-specified thresholds. Various wastewater treatment methods can be employed to achieve this objective. These methods encompass chemical precipitation, ion exchange, membrane filtration, electrochemical treatment technologies, and adsorption. Among these methods, adsorption stands out due to its notable advantages. Some of these advantages include low cost, ease of implementation, and minimal environmental impact.

Table 1. FAO guidelines for heavy metals in irrigation water [4].

Heavy Metal Ion	Recommended maximum concentration (mg/L)	Heavy Metal Ion	Recommended maximum concentration (mg/L)
Al	5.00	Mn	0.20
As	0.10	Mo	0.01
Be	0.10	Ni	0.20
Cd	0.10	Pb	5.00
Co	0.05	Se	0.02
Cr	0.10	Sn	0
Cu	0.20	Ti	0
F	1.00	W	0
Fe	5.00	V	0.10
Li	2.50	Zn	2.00

The adsorption process refers to the phenomenon where the desired substance from a solution is selectively deposited onto the surface of a material known as the adsorbent. Throughout history, a wide range of adsorbent materials has been employed for wastewater treatment. Among these materials, ceramic-based substances have been utilized since ancient times owing to their remarkable adsorption capacity. Presently, researchers are actively involved in the development of materials that exhibit characteristics such as low cost, ease of processing, and high adsorption capacity. The aim is to create advanced adsorbent materials that are efficient and economical for wastewater treatment purposes. Biopolymers are used in many different applications such as adsorption processes due to their chemical properties, easy processability, low cost, biocompatibility, and biodegradability. Alginate is a low-cost, easily processable, biocompatible, and biodegradable polysaccharide obtained from brown algae cells. In addition to these advantages, it contains too many -OH groups in its chemical structure, which increases the adsorption efficiency with secondary interactions with alginates. Furthermore, its chemical structure can be readily modified following the desired properties. Moreover, these advantages, alginates have low thermal resistance, low pH stability, and mechanical strength. These drawbacks can be mitigated by incorporating additional complexing polymers (such as Chitosan, Gelatin, PVA), inorganic particles, and nanofiber reinforcement into the alginate matrix. Alginates can be gelled by chemical and physical methods; if it contains water in its structure, this gel is called hydrogel, if it is dried in an open atmosphere with heat, it is called xerogel, if it is dried by processes such as freeze drying, it is called cryogel, and if it is dried with supercritical fluids, it is called aerogel. Alginate

gels are frequently used in adsorption processes. Different materials are added to increase the adsorption capacity and improve the mechanical, thermal, and low pH stabilization properties.

This review aims to provide a comprehensive overview of recently developed alginate-based adsorbent gel studies. In this review, we delve into various strategies employed to enhance the adsorption capacity of alginate-based gels, shedding light on the physical and chemical modifications implemented. Additionally, this review provides a concise overview of the chemical structure of alginate, highlighting its linear copolymer nature consisting of (1→4)-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues. The relative composition of these residues in the alginate chain influences its physicochemical properties. Furthermore, the review touches upon the adsorption kinetics and isotherms of alginate-based gels. An understanding of adsorption kinetics aids in optimizing the adsorption process by determining the rate at which adsorption occurs. Isotherm models, such as the Langmuir and Freundlich models, are utilized to describe the equilibrium adsorption behaviour of alginate gels and provide valuable insights into the adsorption capacity and affinity. This review offers a comprehensive examination of recently developed alginate-based adsorbent gels. Exploring various strategies to enhance adsorption capacity and elucidating the physical and chemical properties, provides valuable insights for researchers and practitioners working in the field of adsorption science and technology.

2. Adsorption Kinetic Models and Isotherms

The material that adsorbs the target structure on its surface during the adsorption process is called adsorbent material. The adsorption process refers to the accumulation of the target structure on the surface of the adsorbent material. The efficiency in an adsorption process can be calculated by Equation 1;

$$\text{Adsorption Efficiency (\%)} = \left(\frac{C_0 - C_e}{C_0} \right) * 100 \quad (1)$$

Here, C_0 is the initial pollutant concentration (mg. L^{-1}), and C_e is the pollutant concentration in the solution (mg. L^{-1}) in the equilibrium state of the system. The adsorption capacity of the adsorbent can be calculated using Equation 2;

$$q_t = (C_0 - C_t) * \frac{V}{M} \quad (2)$$

In the equation, q_t is the adsorption capacity at a certain time (mg. g^{-1}), C_0 is the initial concentration (mg. L^{-1}), C_t is the concentration of the solution at a certain time (mg. L^{-1}), V is the solution volume (L), and M is the amount of adsorbent (g) indicates. Furthermore, many mechanisms are effective in this

process; these can be physical interactions or chemical interactions. Concentration gradient, diffusion, and chemical interactions can be limiting factors of the adsorption process. Different kinetic modes have been developed to find the limiting factor in an adsorption process. Among the kinetic models, the most widely used are pseudo-first-order and pseudo-second-order. Linearized pseudo-first-order is expressed by Equation 3 [5];

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (3)$$

In this equation, q_e and q_t represent the adsorption capacity (mg. L^{-1}) at equilibrium and “t” moment, respectively, K_1 is the equation constant and t is the time (minute). The pseudo-first-order equation gives the rate of change of ion adsorption with time. K_1 and q_e values were calculated by plotting $\ln(q_e - q_t)$ - t . The linearized version of the pseudo-second-order is expressed by Equation 4 [5];

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

The variables here are the same as the pseudo-first-order equation. In adsorption studies that fit the pseudo-second-order, it is accepted that the rate limiter is chemisorption. K_2 and q_e values are calculated by plotting the change of t/q_t value concerning t . In addition to kinetic models, different Isotherms have been developed to explain the interaction between adsorbent and adsorbance. The two most commonly used isotherms; Langmuir and Freundlich. Langmuir isotherm can be expressed by Equation 5 [6];

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m} \quad (5)$$

Here C_e is the equilibrium concentration (mg. L^{-1}), q_m is the maximum adsorption capacity of the adsorbent (mg. g^{-1}), and K_L is the Langmuir constant. For adsorption studies conforming to the Langmuir model, it can be said that homogeneous adsorption takes place in the monolayer and on the surface of the adsorbent. With Equation 6, the relationship between Freundlich isotherm and experimental data can be examined [6];

$$\log(q_e) = \frac{1}{n_f} \log(C_e) + \log(K_f) \quad (6)$$

Here, unlike the Langmuir isotherm, K_f is the Freundlich constant and n_f is the Freundlich isotherm constant, which gives an idea about the adsorption availability. Processes conforming to the Freundlich isotherm take place in a multilayer and heterogeneous manner. All these processes are explained by examining the fit between experimental data and models. Derived from the integral equation approach, which offers a simple and useful method for investigating adsorption on heterogeneous surfaces composed of energetically different patches distributed throughout the surface, the Langmuir–

Freundlich equation (Equation 7) mathematically expresses this approach [7].

$$\theta_e = \int_0^{\infty} \theta(E, P_e, T) \times \chi(E) dE \quad (7)$$

Here, $\theta(E, P_e, T)$ represents a classical isotherm for adsorption on each patch with identical sites and the same adsorption energy E , while $\chi(E)$ is a normalized differential energy distribution function. Figure 1 gives a schematic representation of the energy distribution of adsorption on homogeneous and heterogeneous surfaces of a porous adsorbent material.

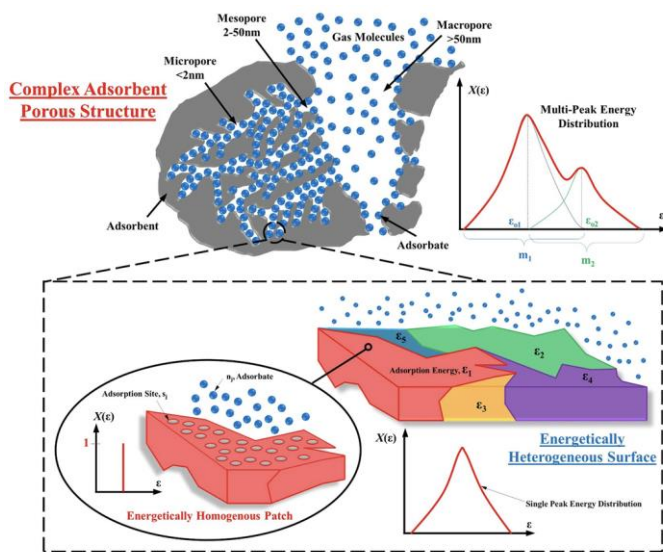


Figure 1. Schematic representation of the energy distribution of heterogeneous and homogeneous surfaces occurring on the surface of the porous adsorbent material [8].

In addition to all these, parameters such as temperature, time, solid-liquid ratio, and pH are effective in the adsorption process, and the effect of these parameters on the process should be examined. The effect of temperature on adsorption significantly affects both the adsorption rate and capacity. The adsorption rate increases strongly as the temperature increases due to the increasing kinetic energy of the adsorbate molecules [9]. However, adsorption capacity may decrease as temperature increases; this indicates that there is an exothermic process and the adsorptive forces between the active sites on the adsorbent surface and the pollutant material are weakened [9]. If the adsorption process is an endothermic reaction, the adsorption capacity will tend to increase [10]. Thermodynamic parameters (enthalpy, entropy, and Gibbs free energy) can be estimated from adsorption data, providing insights into adsorption mechanisms and can be used for process modification and optimization. In addition, the pH of the solution significantly affects the adsorption process, affecting both the surface charge of the adsorbent and the adsorption mechanisms [11]. The surface charge can be

positive or negative depending on pH, and this charge is critical to the adsorption process. The point of zero charge (PZC), where the surface of the adsorbent is neutral, is important as it determines the surface chemistry and reactivity [11]. By changing ion adsorption, pH affects the availability and speciation of ions and also affects the hydrolysis and complexation reactions between metal ions and the adsorbent, thus changing the adsorption efficiency. Additionally, pH changes the adsorption rate and capacity by affecting the kinetic energy of adsorbate molecules and the availability of adsorption sites on the adsorbent surface. This is particularly important for applications such as heavy metal removal and biosorption, because optimizing pH can significantly increase adsorption efficiency and effectiveness.

3. Alginate as a Biopolymer

Natural polymer-based adsorbents offer a promising alternative to conventional adsorbents in renewability, recyclability, and tunable physicochemical properties [12]. Alginate, lignin, cellulose, and chitosan are generally low-cost biopolymers. Due to its high biodegradability, biocompatibility, and environmentally friendly nature, alginate is widely used as adsorbent material for different inorganic and organic pollutants. However, the low-temperature thermal degradation of sodium alginate [13] and poor stability [14] limit its use in different applications. Therefore, it is necessary to develop alginate to remove pollutants from wastewater.

Alginate refers to a family of linear polysaccharides, such as alginic acid and alginate salts, composed of β (1 \rightarrow 4) linked β -D-mannuronic acid (M) residues and the C-5 epimer α -L-guluronic acid (G). These monomers are arranged in an irregular block, consisting of homo-sequences of consecutive M or G residues (M- or G-blocks) alternating with G/M hetero-sequences (see Figure 2). While M blocks add flexibility to the alginate structure, G blocks increase the rigidity of the alginate. Besides Mw, G/M ratio also affects the properties of alginate-based gels. The G/M ratio and Mw must be considered when examining the properties of alginate-based gels to be produced.

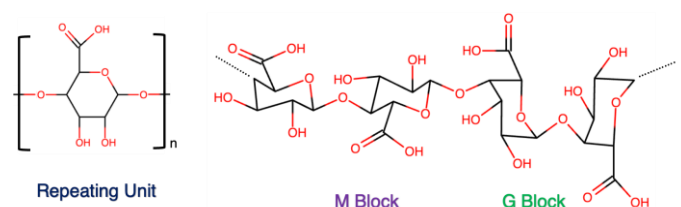


Figure 2. Chemical structure of alginate.

Alginate can be produced from brown algae cells in various forms. Sodium alginate is the form of alginate obtained from brown algae cells and is the sodium salt of alginic acid. It is

possible to extract alginate from brown algae cells as alginic acid, sodium alginate and calcium alginate. The extraction of alginate from seaweed is a multi-stage process that begins with washing, drying, and milling the seaweed, followed by rehydration and chemical treatments to remove unwanted compounds, then applying acid or alkali pre-treatment to break the plant cell wall and using sodium carbonate extraction to obtain water-soluble alginate, and finally recovering the alginate from the solution through sodium alginate, calcium alginate, or alginic acid precipitation methods [15]. Alginate extraction routes are presented in Figure 3.

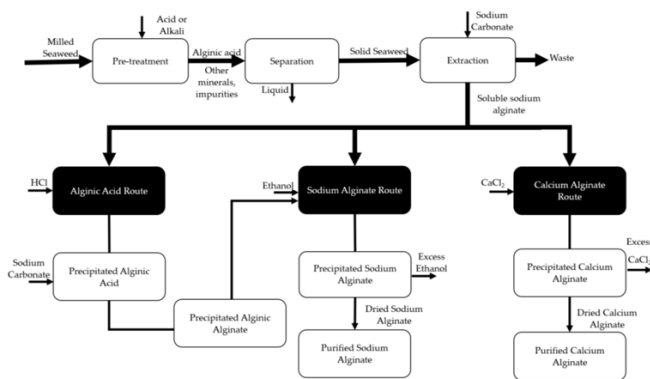


Figure 3. Alginate extraction routes from brown seaweed [15].

Alginates can form gels. Gelation can occur by ionotropic gelation or acid precipitation. Ionotropic gelation occurs when the negatively charged carboxyl parts of the alginate chains interact with multivalent cations or cationic polymers. The aqueous alginate solution, also called the "sol" phase, can be crosslinked by both divalent and trivalent cations [16]. Cross-linking of alginate leads to a "left to gel" transition resulting in the formation of alginate hydrogels that retain high water molecule content via hydrogen bonds [17]. The gelation kinetics and properties of the obtained hydrogels are mainly dependent on the properties of the ion such as valence electron and radius [18].

The interaction between polyvalent cations and alginate is described by the "eggbox" model. It is thought that electronegative vacancies, which can accommodate the cations of two G blocks consisting of adjacent chains, form "eggbox junctions" [19]. Before the crosslinking step, the "eggbox junctions" are occupied by alginate counterions such as sodium [20]. As a result of ion exchange, an "egg box" structure is formed. Although it is thought that only G blocks are involved in intermolecular crosslinking, MGM blocks may also contribute to gelation as a result of weak interactions with cations [21]. The egg box structure is given in Figure 4.

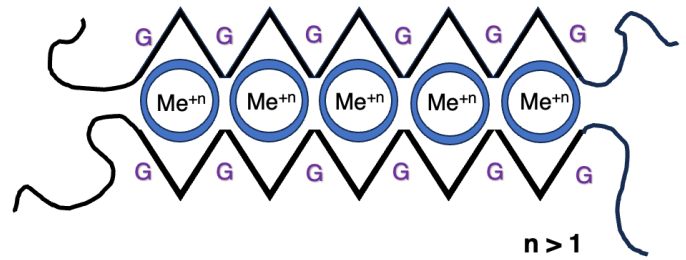


Figure 4. Egg-Box structure.

While the alginate solution is in its sol phase, different materials can be added to increase its performance. After doping the gels, it is passed from the sol to the gel. In this way, high-performance alginate-based hydrogels can be produced. These additives can be organic polymers, synthetic polymers, inorganic particles, or a combination of them. For example, while complex gels are formed by adding chitosan to increase the pH resistance of alginate, gelatin, and PVA to improve their mechanical properties, their properties can be improved by adding metallic or ceramic-based nanoparticles with different properties. In this mini-review, wastewater treatment studies by doping magnetic, photocatalytic, and clay-based materials into alginate or alginate complex gels are included. In the subsequent sections of the mini-review, a comprehensive analysis is provided regarding the elimination of organic and inorganic contaminants from wastewater using alginate-based gels that have undergone the gelation process.

4. Magnetic Particle Doped Alginate Gels

Adsorbent materials must be separated from the solution after removing the target compounds in the wastewater. Although the separation of macro-size (around cm-mm size) beads can still be easily separated by filtration methods, it is relatively difficult to separate micro and nano-size beads from the wastewater solution with filtration methods. The external magnetic field is acceptable as a promising easy and inexpensive method for separating adsorbent materials from wastewater solution. The addition of magnetic materials (Fe, Fe₃O₄, etc.) in gels with an alginate-based matrix ensures that these gels can be easily separated via the external magnetic field from the solution after the adsorption process. In their study, Ma et al. investigated the removal of dyes from wastewater through the incorporation of graphene oxide (GO) and iron oxide nanoparticles (Fe₃O₄) into alginate/chitosan gels [22]. Their findings revealed that the various functional groups present in the structure of GO are adsorbed onto the gels through secondary interactions with the dyes present in the wastewater. The inclusion of Fe₃O₄ was found to facilitate the subsequent solid/liquid separation process after adsorption. The researchers observed that the addition of GO and chitosan led to an increase in the surface area and porosity of the gels. However, the increased amount of chitosan had a negative

impact on the adsorption process. They attributed this phenomenon to the enhanced interaction between alginate and chitosan, which resulted in reduced penetration of the dye into the gel. Furthermore, the authors demonstrated that the adsorption process followed the pseudo-first-order kinetics, indicating that physical adsorption predominated. They also noted that the gels maintained their high adsorption capacity even after five cycles, suggesting their durability and potential for repeated use. Also, with the addition of magnetic material in this study, extra materials are used to increase the adsorption capacity of the gels. Zeng et al. reported that they developed adsorbent material by adding Fe_3O_4 /maghemite nanoparticles into alginate/chitosan matrix aerogels [23]. They added iron mud as the main adsorption agent into the gel matrix. They studied the removal of phosphate ions in wastewater and observed time-varying adsorption kinetics. In this study, it was tried to eliminate the weak properties of alginate by using chitosan in addition to alginate. In addition to chitosan, different polymeric structures are also used to improve the properties of alginate. Zang et al. produced alginate/PVA hydrogels with the interpenetrating method in their work [24]. They claimed that the addition of PVA would increase the stability of the gels. They prepared PVA and sodium alginate solution and emulsified with Tween 80, Span 80, and Cyclohexane to form a microsphere. They added Fe^{2+} and Fe^{3+} ions to the solution they obtained, and then, by the addition of NH_4OH , the Fe_3O_4 particles were precipitated. They claimed that when $\text{Fe}^{2+/3+}$ ions were added and interacted with the carboxyl groups in the alginate, so they obtained smaller particles during precipitation. They studied the adsorption of different aromatic compounds from wastewater, such as salicylic acid, phenol, aniline, p-methoxy phenol, and p-nitrophenol, with the Fe_3O_4 added SA/PVA gel they obtained. They calculated the lowest adsorbent capacity at pH 7 with salicylic acid (almost 0 mg/g) and the highest adsorbent capacity when working with p-nitrophenol (78 mg/g). They claimed that this was due to the interaction of different aromatic compounds with the hydrophilic and hydrophobic parts of the gels. However, they explained that the adsorbent capacity varies at different pHs, and since the gels always have a negative zeta potential value in the pH 1-13 band, the alginate carboxylate groups change with pH, which is due to the change in hydrophilicity and hydrophobicity.

Furthermore, the weak mechanical properties of alginate can also be increased with different nanofiber reinforcements. Nanofibers increase the mechanical strength of nano-fiber composite gels by carrying the mechanical strength of the matrix. Salahuddin et al. reported that they carried out a wastewater (red mud solution) cleaning process by adding decorated cellulose nanofiber and Fe_3O_4 nanoparticles into the alginate hydrogel matrix [25]. They reported that the addition of cellulose nanofibers increased the mechanical strength of

the gels. In addition, they noticed that the addition of Fe_3O_4 nanoparticles, produced by the co-precipitation method, with CNF to the alginate matrix increased the surface area and porosity of the gels. They reported that the addition of Fe_3O_4 nanoparticles had a positive effect on the wastewater treatment process, and that solid/liquid separation could be made easily by applying an external magnetic field after the process.

In a different approach, the properties of alginate gels can be improved by crosslinking with different agents instead of alginate Ca^{2+} ions. Wang et al. produced magnetic alginate-based aerogel with the addition of Fe_3O_4 in their gels, which is obtained by crosslinking sodium alginate with industrial alkaline residues [26]. They showed that crosslinking alginate with industrial alkaline residues provides a more homogeneous pore distribution during freeze drying, increases mechanical strength, and increases the adsorption efficiency. They attributed this to the fact that different metal ions in the alkaline residue show different gelation properties and that internal gelation occurs more slowly and homogeneously. They carried out Cd (II) removal from wastewater; they claimed that the adsorption kinetics were compatible with the pseudo-second-order, and the isotherm compatible with Langmuir. They repeated the process for 5 cycles and observed that around 90% of the material retained its effect.

The surfaces of the gels produced in the nanoscale can be modified by polymerization methods, which can lead to an increase in the adsorption capacity of the gels. Wu et al., in their study, coated $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ nanoparticles with alginate and gelled them with Ca^{2+} ions [27]. They modified the surfaces of the gels they produced with poly (ethylene imine) and polymerized benzyl dimethyl [2-[(2-methyl-1-oxoallyl)oxy] ethyl] (BDAC) ammonium chloride by free radical polymerization. They tried the adsorption of Diclofenac Sodium and Reactive Red X-3 compounds from wastewater with the presence of various functional groups of BDAC. They emphasized that the adsorption capacity of the gels increased significantly with the addition of BDAC. They showed that the isotherm of the adsorption process is compatible with Langmuir, and its kinetics with pseudo-second-order. They examined the interaction between adsorbent and adsorbed by FTIR and XPS analysis. They showed that the adsorption resulted from the electrostatic action, hydrogen bonding, and π - π interactions between the gel and the adsorbed.

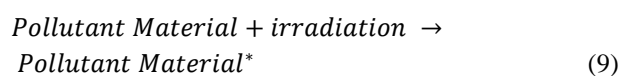
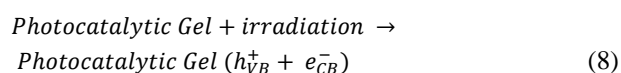
Furthermore, the coating of nano-sized particles with different polymers is encountered in gels produced later in the form of polyelectrolyte with alginate in literature. Wang et al., in their study, coated Fe_3O_4 nanoparticles, which they produced with co-precipitation, with APTES [28]. With the presence of functional groups of the particles modified with APTES, they formed a polyelectrolyte with sodium alginate. The obtained complex structure was crosslinked with Ca^{2+} ions. Gradual

APTES and alginate coating of Fe₃O₄ particles increased the surface area and decreased the magnetic saturation value. They tried the removal of Pb²⁺ ions from wastewater and obtained an adsorbent capacity of 105.8 mg/g. They showed that the isotherm of the adsorption process was compatible with Langmuir, and the kinetic of the adsorption process was consistent with the pseudo-second-order. They performed adsorption with HCl acid and claimed that the material worked with 77% efficiency from 5 cycles.

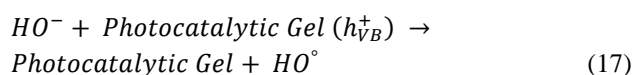
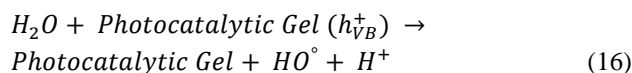
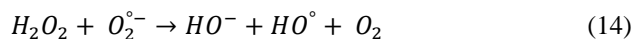
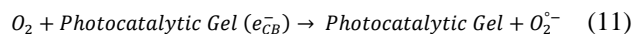
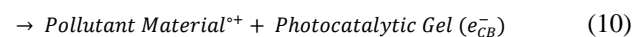
Moreover, the magnetic particles provide easy separation of the gels from the solution, as well as increase the adsorption efficiency with the magnetic fields of the particles. The interaction of the ions in the solution (due to their charge) with the magnetic field has a positive effect on the adsorption capacity of the gels containing magnetic particles. Uysal et al. investigated the adsorption of Nd³⁺ ions from wastewater using Fe-based particles incorporated into alginate gels under the influence of a magnetic field [10]. To enhance the stability of the alginate-based gels under low pH conditions, chitosan was utilized as a coating agent. The adsorption process exhibited varying kinetic models at different time intervals. Initially, the adsorption followed a pseudo-first-order kinetic model, which later transitioned to a pseudo-second-order model. Toward the end of the adsorption process, the Elovich equation provided a suitable fit for the experimental data. The authors demonstrated that chemisorption played a dominant role in the adsorption process. The adsorption isotherm conformed to the Freundlich isotherm model, indicating heterogeneous adsorption involving multiple layers. Additionally, desorption studies were conducted, revealing that HCl acid exhibited the highest efficiency, while tartaric acid, an organic acid, showed promising results. The authors attributed this phenomenon to the complexation between tartaric acid and rare earth elements (REEs).

5. Photocatalytic Particle Doped Alginate Gels

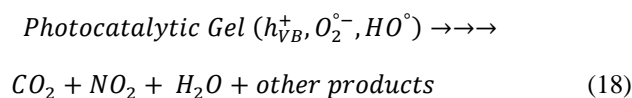
Adding materials with photocatalytic properties into gels is an effective method for removing contaminants from the waste solution under solar and UV irradiation. Photocatalytic materials cause the scattering of rays of certain wavelengths with their band gaps. Photocatalytic degradation can be briefly expressed by the following Equation 8-18 [29];



Pollutant Material + Photocatalytic Gel*



Pollutant Material +



Irradiation of sunlight and UV onto photocatalytic gels leads to the formation of charge carriers and the transport of electron and hole pairs ($e_{CB}^-/h\nu_{VB}^+$). The pollutant structure, on the other hand, adsorbed on the surface of the photocatalytic gel absorbs energy and transfers the photogenerated electron to the conduction band of the gel. In interaction with these photogenerated electrons, surface-adsorbed oxygen (O₂) molecules are converted into superoxide radical anions (O₂^{•-}) and hydrogen peroxide radicals (HOO[•]). In addition, photogenerated holes ($h\nu_{VB}^+$) combine with water molecules or hydroxyl anions on surfaces to form hydroxyl radicals (HO[•]) as a result of photocatalytic excitation. This photogenerated species attacks the structure of the pollutant to convert active radical species into non-toxic molecules. The point to be considered in adsorption experiments is that performing the reaction under irradiation after adsorption in the dark without irradiation increases the yield.

TiO₂ nanoparticles are used in various applications as photocatalysts due to the band gap of structure. Chkirida et al., in their study, produced Ca alginate gels, added clay into the gels, coated the surface of the gels with TiO₂-P25 nanoparticles via non-thermal impregnation method, and reported that they removed Methylene Blue from wastewater under UV light [30]. Their gels' excellent photocatalytic function was proven by testing their ability to degrade COD (Chemical Oxygen Demand), a typical indication of organic contaminants in water. The COD is the quantity of oxygen required to oxidize the organic components in the water sample. They showed increased COD removal with UV light. Also, Dai et al. produced calcium alginate aerogels, furthermore they added TiO₂ nanoparticles to the alginate gel

matrix in their study [31]. With the addition of TiO_2 , the pore size and surface area of the gels increased, and the UV resistance also increased. They tried to the separation of oil/water from wastewater with the gels they produced. They separated around 99% of soybean oil, hexane, kerosene, and pump oils from water. They also tried the adsorption of methylene orange (MO) via using UV irradiation, and they removed around 98% MO from wastewater. They claimed that even after 6 cycles of UV adsorption, the gels remained stable to a large extent. Moreover, doping TiO_2 particles causes an increase in photocatalytic properties. Chkirida et al. reported that by doping Fe_2O_3 and Fe_3O_4 to TiO_2 nanoparticles, they improved the photocatalytic properties of TiO_2 nanoparticles [32]. They produced calcium alginate microspheres containing $\text{TiO}_2\text{-Fe}_2\text{O}_3$ and $\text{TiO}_2\text{-Fe}_3\text{O}_4$ in 4 different ratios (1%, 2.5%, 5%, and 10%). They tried to remove MB from the wastewater with the gels produced, and they claimed that 80% of the wastewater was cleaned.

In addition to materials with suitable band gaps such as TiO_2 , different materials are also used as photocatalysts. Materials with overlapping conduction and valence bands (without band gap), such as Ag nanoparticles, can radiate at certain wavelengths. This phenomenon is called surface plasmon resonance. Thanks to the electron configuration of noble metals, this radiation can be controlled by the number of electrons on the surface, which varies according to particle size and surface area. Ag nanoparticles are a material that exhibits photocatalytic properties with the phenomenon of surface plasmon resonance. For this reason, Ag nanoparticles are also used as an alternative to TiO_2 particles in wastewater cleaning processes. Hasan et al., in their study, produced complex gels with alginate and polyacrylonitrile and reported their findings on the removal of nitrophenols (DNP) compounds from wastewater by Ag nanoparticles in their gels [33]. They prepared a solution with sodium alginate precursor powder, then added AgNO_3 into the solution. After the reduction of metallic Ag nanoparticles in the solution was completed, acrylonitrile monomer and N, N-methylene bisacrylamide (crosslinker) were added to the solution, respectively. After completing the structural characterization of the complex gels, they produced, they used the response surface method to determine the most optimal parameters in the removal process of their compounds in wastewater. They claimed that a photocatalytic capacity of 99.46% could be obtained when the irradiation time was 35 minutes, the pH of the DNP solution was 4.68, and the DNP concentration was 70 mg L^{-1} .

6. Clay Particle Doped Alginate Gels

Clay-based materials are used in various applications due to their physical and chemical properties. Clay-based materials are frequently used in adsorption processes. Their chemical structures, crystal structures, and ionic charge balances make

ceramic-based materials good adsorbent materials. They can adsorb on their surfaces by secondary interactions (such as Van der Waals, hydrogen bonds, etc.) with many materials such as water and organic-based structures. Also, their porous structure positively affects the adsorption capacity. Mundkur et al. reported doping clay materials into calcium alginate gels in different forms [34]. They produced clay-alginate beads, sodium carbonate-treated clay-alginate beads, clay-alginate-surfactant beads, and clay-alginate-nanoparticle (Fe_3O_4) beads and studied MB removal from wastewater. They achieved the removal of around 95% of MB in wastewater with the gels they produced, and they claimed that the adsorption kinetics fitted pseudo-second-order and isotherm compatible with Langmuir.

The montmorillonite crystal structure consists of 2 silica tetrahedral sheet sandwiches, the octahedral aluminum sheet of the middle part, and is also a ceramic material group with high water absorption capacity. Its chemical structure consists of Si, Al, Ca, Na, and Mg. Akin et al., in their studies, produced gelatin-alginate complex gel and doped montmorillonite and removed crystal violet from wastewater [35]. They prepared gelatin and sodium alginate solution, then added montmorillonite to this solution and homogenized it, then added it to the CaCl_2 solution. They optimized the optimum pH, temperature, and time for adsorption. They stated that the maximum adsorption capacity was reached for 120 minutes and it was suitable for adsorption at pH 7. They claimed that the adsorption isotherm is Langmuir, so the adsorption takes place homogeneously from mono-layer, and its kinetics is pseudo-second-order, that is adsorption by chemical interaction. They reported that the adsorption efficiency was 90.2% in the first cycle and that the yield decreased by 66.8% at the end of the 10th cycle.

Bentonite is a ceramic material group consisting of Ca and Na montmorillonite, with high water absorption capacity and high adsorbent capacity. According to Yari et al., bentonite/ Fe_3O_4 nanoparticles and sodium alginate may efficiently adsorb lead ions [36]. Four kinds of bentonite magnetic nanoparticles were produced in this work. Magnetic nanoparticles were then adsorbed on alginate to form beads for removing lead ions from synthetic pollution solutions. Adsorbent dose, pH values, stirring speeds, pollutant concentrations, and adsorption periods were all examined. The results show that 0.1 g of beads at a pH of 7, an adsorption duration of 8 hours, and a stirring velocity of 100 rpm provided the best conditions for removing Pb^{2+} . The beads showed a high adsorption efficiency of around 98%, and the adsorption process followed the Freundlich isotherm model. All alginate gels described in this review and their performance are summarized in Table 2.

Table 2. Different alginate-based gels and their adsorbent capacities.

Matrix	Additive	Pollutant Material	Adsorption Capacity (mg/g)	Reference
Sodium Alginate/ Chitosan	GO, Fe ₃ O ₄	MB	21.325	16
		NR	44.654	
		ST	44.313	
Alginate/ Chitosan	Fe ₃ O ₄ , Fe ₂ O ₃	Phosphate	18.5	17
Alginate/ PVA	Fe ₃ O ₄	Aromatic Compounds	5-78	18
Alginate	CNF, Fe ₃ O ₄	Al	22	19
		K	13.2	
		Se	19	
		Na	11.1	
		V	44.4	
S	13.7			
Alginate/Alkaline Residue	Fe ₃ O ₄	Cd	38.83	20
Sodium alginate/enzylidimethyl[2-[(2-methyl-1-oxoallyl) oxy] ethyl] ammonium chloride	Fe ₃ O ₄ @SiO ₂	DS	340.58	21
		X-3B	370.85	
Sodium Alginate/APTES	Fe ₃ O ₄	Pb	105.8	22
Alginate/ Chitosan	Fe	Nd	6.72	23
Alginate	Clay-TiO ₂	MB	-	25
Alginate	TiO ₂	Oil	-	26
Alginate	Fe ₃ O ₄ and Fe ₂ O ₃ Doped TiO ₂	MB	-	27
Alginate-g-Polyacrylonitrile	Ag	Nitrophenols	-	28
Alginate	Different Clays	MB	-	29
Sodium Alginate/ Gelatin	Montmorillonite	Crystal Violet	1000	30
Alginate	Bentonite, Fe ₃ O ₄	Pb	-	31

7. Future Outlook

Due to its properties, alginate is a promising biopolymer in adsorption processes. With different doping, functional properties can be gained and adsorption efficiency can be increased. Alginate properties are improved with modifications made by chemical reactions and the addition of another complexing polymer, apart from doping. It is predicted that access to clean water will become increasingly difficult in the coming years. Wastewater, arising from the anthropogenic activities that have been established by humanity, necessitates treatment before its discharge into the natural environment. Alginate gels are promising in industrial-scale wastewater

treatment processes due to their biodegradable and bioluminescent nature, low cost, and easy production.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] N. A. A. Qasem, R. H. Mohammed, ve D. U. Lawal, "Author Correction: Removal of heavy metal ions from wastewater: a comprehensive and critical review", *npj Clean Water*, c. 4, sy 1, s. 52, Ara. 2021, doi: 10.1038/s41545-021-00144-z.
- [2] B. F. Bakare ve G. C. Adeyinka, "Evaluating the Potential Health Risks of Selected Heavy Metals across Four Wastewater Treatment Water Works in Durban, South Africa", *Toxics*, c. 10, sy 6, s. 340, Haz. 2022, doi: 10.3390/toxics10060340.
- [3] S. Mandal, A. Kunhikrishnan, N. S. Bolan, H. Wijesekara, ve R. Naidu, "Application of Biochar Produced From Biowaste Materials for Environmental Protection and Sustainable Agriculture Production", içinde *Environmental Materials and Waste*, Elsevier, 2016, ss. 73-89. doi: 10.1016/B978-0-12-803837-6.00004-4.
- [4] "A compendium of standards for wastewater reuse in the Eastern Mediterranean Region", World Health Organization, 2006.
- [5] H. Qiu, L. Lv, B. Pan, Q. Zhang, W. Zhang, ve Q. Zhang, "Critical review in adsorption kinetic models", *J. Zhejiang Univ. Sci. A*, c. 10, sy 5, ss. 716-724, May. 2009, doi: 10.1631/jzus.A0820524.
- [6] M. A. Al-Ghouthi ve D. A. Da'ana, "Guidelines for the use and interpretation of adsorption isotherm models: A review", *Journal of Hazardous Materials*, c. 393, s. 122383, Tem. 2020, doi: 10.1016/j.jhazmat.2020.122383.
- [7] S. Azizian ve S. Eris, "Adsorption isotherms and kinetics", içinde *Interface Science and Technology*, c. 33, Elsevier, 2021, ss. 445-509. doi: 10.1016/B978-0-12-818805-7.00011-4.
- [8] K. C. Ng, M. Burhan, M. W. Shahzad, ve A. B. Ismail, "A Universal Isotherm Model to Capture Adsorption Uptake and Energy Distribution of Porous Heterogeneous Surface", *Sci Rep*, c. 7, sy 1, s. 10634, Eyl. 2017, doi: 10.1038/s41598-017-11156-6.
- [9] T. M. Budnyak vd., "Chitosan Deposited onto Fumed Silica Surface as Sustainable Hybrid Biosorbent for Acid Orange 8 Dye Capture: Effect of Temperature in Adsorption Equilibrium and Kinetics", *J. Phys. Chem. C*, c. 124, sy 28, ss. 15312-15323, Tem. 2020, doi: 10.1021/acs.jpcc.0c04205.
- [10] E. Uysal, E. Emil-Kaya, D. Yesiltepe-Ozcelik, ve S. Gurmen, "Nd Recovery from Wastewater with Magnetic Calcium Alginate ((1,4)-β-d-Mannuronic Acid and α-L-Guluronic Acid) Hydrogels", *ACS Omega*, c. 8, sy 19, ss. 16762-16778, May. 2023, doi: 10.1021/acsomega.2c08221.
- [11] M. Kosmulski, "The pH dependent surface charging and points of zero charge. IX. Update", *Advances in Colloid and Interface Science*, c. 296, s. 102519, Eki. 2021, doi: 10.1016/j.cis.2021.102519.
- [12] O. Duman, T. G. Polat, C. Ö. Diker, ve S. Tunç, "Agar/κ-carrageenan composite hydrogel adsorbent for the removal of Methylene Blue from water", *International Journal of Biological Macromolecules*, c. 160, ss. 823-835, Eki. 2020, doi: 10.1016/j.ijbiomac.2020.05.191.
- [13] Y.-N. Phang, S.-Y. Chee, C.-O. Lee, ve Y.-L. Teh, "Thermal and microbial degradation of alginate-based superabsorbent polymer", *Polymer Degradation and Stability*, c. 96, sy 9, ss. 1653-1661, Eyl. 2011, doi: 10.1016/j.polydegradstab.2011.06.010.
- [14] Y. Liu vd., "Photoreduction of Cr(VI) from acidic aqueous solution using TiO₂-impregnated glutaraldehyde-crosslinked alginate beads and the effects of Fe(III) ions", *Chemical Engineering Journal*, c. 226, ss. 131-138, Haz. 2013, doi: 10.1016/j.cej.2013.04.048.
- [15] S. Saji, A. Hebden, P. Goswami, ve C. Du, "A Brief Review on the Development of Alginate Extraction Process and Its Sustainability",

- Sustainability, c. 14, sy 9, s. 5181, Nis. 2022, doi: 10.3390/su14095181.
- [16] S. Boi vd., "Alginate microbeads with internal microvoids for the sustained release of drugs", *International Journal of Biological Macromolecules*, c. 156, ss. 454-461, Ağu. 2020, doi: 10.1016/j.ijbiomac.2020.04.083.
- [17] B. Reig-Vano, B. Tytkowski, X. Montané, ve M. Giamberini, "Alginate-based hydrogels for cancer therapy and research", *International Journal of Biological Macromolecules*, c. 170, ss. 424-436, Şub. 2021, doi: 10.1016/j.ijbiomac.2020.12.161.
- [18] S. H. Ching, N. Bansal, ve B. Bhandari, "Alginate gel particles—A review of production techniques and physical properties", *Critical Reviews in Food Science and Nutrition*, c. 57, sy 6, ss. 1133-1152, Nis. 2017, doi: 10.1080/10408398.2014.965773.
- [19] D. Dhamecha, R. Movsas, U. Sano, ve J. U. Menon, "Applications of alginate microspheres in therapeutics delivery and cell culture: Past, present and future", *International Journal of Pharmaceutics*, c. 569, s. 118627, Eki. 2019, doi: 10.1016/j.ijpharm.2019.118627.
- [20] D. Hudson ve A. Margaritis, "Biopolymer nanoparticle production for controlled release of biopharmaceuticals", *Critical Reviews in Biotechnology*, c. 34, sy 2, ss. 161-179, Haz. 2014, doi: 10.3109/07388551.2012.743503.
- [21] S. N. Pawar ve K. J. Edgar, "Alginate derivatization: A review of chemistry, properties and applications", *Biomaterials*, c. 33, sy 11, ss. 3279-3305, Nis. 2012, doi: 10.1016/j.biomaterials.2012.01.007.
- [22] J. Ma vd., "Magnetic graphene oxide-containing chitosan-sodium alginate hydrogel beads for highly efficient and sustainable removal of cationic dyes", *International Journal of Biological Macromolecules*, c. 193, ss. 2221-2231, Ara. 2021, doi: 10.1016/j.ijbiomac.2021.11.054.
- [23] H. Zeng vd., "Iron-loaded magnetic alginate-chitosan double-gel interpenetrated porous beads for phosphate removal from water: Preparation, adsorption behavior and pH stability", *Reactive and Functional Polymers*, c. 177, s. 105328, Ağu. 2022, doi: 10.1016/j.reactfunctpolym.2022.105328.
- [24] M.-K. Zhang, X.-H. Zhang, ve G.-Z. Han, "Magnetic alginate/PVA hydrogel microspheres with selective adsorption performance for aromatic compounds", *Separation and Purification Technology*, c. 278, s. 119547, Ara. 2021, doi: 10.1016/j.seppur.2021.119547.
- [25] B. Salahuddin vd., "Magnetic Hydrogel Composite for Wastewater Treatment", *Polymers*, c. 14, sy 23, s. 5074, Kas. 2022, doi: 10.3390/polym14235074.
- [26] S.-J. Wang vd., "Floatable magnetic aerogel based on alkaline residue used for the convenient removal of heavy metals from wastewater", *Chemical Engineering Journal*, c. 399, s. 125760, Kas. 2020, doi: 10.1016/j.cej.2020.125760.
- [27] Y. Wu vd., "Construction of magnetic alginate-based biosorbent and its adsorption performances for anionic organic contaminants", *Separation and Purification Technology*, c. 297, s. 121566, Eyl. 2022, doi: 10.1016/j.seppur.2022.121566.
- [28] J. Wang vd., "Production of magnetic sodium alginate polyelectrolyte nanospheres for lead ions removal from wastewater", *Journal of Environmental Management*, c. 289, s. 112506, Tem. 2021, doi: 10.1016/j.jenvman.2021.112506.
- [29] M. Mavaei, A. Chahardoli, Y. Shokoohinia, A. Khoshroo, ve A. Fattahi, "One-step Synthesized Silver Nanoparticles Using Isoimperatorin: Evaluation of Photocatalytic, and Electrochemical Activities", *Sci Rep*, c. 10, sy 1, s. 1762, Şub. 2020, doi: 10.1038/s41598-020-58697-x.
- [30] S. Chkirida vd., "Highly synergic adsorption/photocatalytic efficiency of Alginate/Bentonite impregnated TiO₂ beads for wastewater treatment", *Journal of Photochemistry and Photobiology A: Chemistry*, c. 412, s. 113215, May. 2021, doi: 10.1016/j.jphotochem.2021.113215.
- [31] J. Dai vd., "TiO₂-alginate composite aerogels as novel oil/water separation and wastewater remediation filters", *Composites Part B: Engineering*, c. 160, ss. 480-487, Mar. 2019, doi: 10.1016/j.compositesb.2018.12.097.
- [32] S. Chkirida, N. Zari, R. Achour, A. E. K. Qaiss, ve R. Bouhfid, "Effect of iron doped titanium oxide encapsulated in alginate on photocatalytic activity for the removal of dye pollutants", *RSC Adv.*, c. 10, sy 38, ss. 22311-22317, 2020, doi: 10.1039/D0RA02898C.
- [33] I. Hasan, C. Shekhar, W. Alharbi, M. Abu Khanjer, R. A. Khan, ve A. Alsalmé, "A Highly Efficient Ag Nanoparticle-Immobilized Alginate-g-Polyacrylonitrile Hybrid Photocatalyst for the Degradation of Nitrophenols", *Polymers*, c. 12, sy 12, s. 3049, Ara. 2020, doi: 10.3390/polym12123049.
- [34] N. Mundkur, A. S. Khan, M. I. Khamis, T. H. Ibrahim, ve P. Nancarrow, "Synthesis and characterization of clay-based adsorbents modified with alginate, surfactants, and nanoparticles for methylene blue removal", *Environmental Nanotechnology, Monitoring & Management*, c. 17, s. 100644, May. 2022, doi: 10.1016/j.enmm.2022.100644.
- [35] K. Akin, V. Ugraskan, B. Isik, ve F. Cakar, "Adsorptive removal of crystal violet from wastewater using sodium alginate-gelatin-montmorillonite ternary composite microbeads", *International Journal of Biological Macromolecules*, c. 223, ss. 543-554, Ara. 2022, doi: 10.1016/j.ijbiomac.2022.11.002.
- [36] M. Yari, P. Derakhshi, K. Tahvildari, ve M. Nozari, "Preparation and Characterization of Magnetic Iron Nanoparticles on Alginate/Bentonite Substrate for the Adsorptive Removal of Pb²⁺ Ions to Protect the Environment", *J Polym Environ*, c. 29, sy 7, ss. 2185-2199, Tem. 2021, doi: 10.1007/s10924-020-02028-8.