Chapter

Polymer Hydrogels for Wastewater Treatment

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Abstract

The pollution of water resources turns into a worldwide problem because of the indiscriminate disposal of pollutants both organic and inorganic in nature. It stays hard to manner or control the purification of wastewater before it flows to water reservoirs. The growing interest in the improvement and application of novel hydrogels in wastewater remedy is due to its particular chemical characteristics along with hydrophilicity, sensitivity, and functionality. Hydrogels exhibit superior overall performance inside the adsorptive removal of a wide variety of aqueous pollutants along with heavy metals, nutrients, and toxic dyes. In this chapter, we are focusing on the behavior and importance of the hydrogels used so far for the removal of both organic and inorganic pollutants from wastewater. With this contribution, we will be able to elaborate the answer for why these hydrogels are superior than other materials used for the same purpose. More attention is given to the removal of heavy metal ions from wastewater using different hydrogel systems.

Keywords: hydrogels, hydrophilicity, sensitivity, heavy metal ions, water treatment

1. Introduction

In recent times, the fast growth of industries has caused critical troubles within the natural environment. The effluents of many industries that include paint industries, metal plating, food industries, pharmaceutical industries, and battery production, which comprise heavy metallic ions, dyes, and organic materials, are discharged without delay into water bodies and cause water pollution. These pollutants above the permissible limit cause serious effects on human beings and other terrestrial and aquatic animals. These substances penetrate and accumulate inside the bodies through food chains [1]. For the remediation and purification of waste-contaminated water, a number of different strategies were used, which include chemical precipitation [2], ion exchange [3], biological methods [4], membrane separation [5], reverse osmosis [6], coagulation and flocculation [7], catalysis [8–11], photodegradation [12], and adsorption [13, 14]. Among these strategies, adsorption is considered a cheap, quick, and environmental friendly process for wastewater treatment.

Generally, the adsorption process is broadly categorized in chemisorption and physisorption. Chemisorption also called chemical adsorption involves the formation of a chemical bond between adsorbate and adsorbent and therefore behaves as an irreversible system. Physisorption or physical adsorption takes place through physical interaction like hydrogen bonding, van der Waals, and hydrophobic interactions between adsorbate and adsorbent and acts in a reversible manner. Physical
conditions such as pH, ionic energy, adsorbate and adsorbent dosage, contact time, and temperature are the most vital factors that affect the adsorption capability of hydrogels. The optimization of these factors is very crucial and should be considered first to layout the adsorption process at large scale [15, 16].

Hydrogels are three-dimensional, cross-linked, and flexible polymer networks having hydrophilic groups like hydroxyl, carboxyl, and amide [17] that swell in water and biological fluids. This swelling property is reversible and depends strongly upon environmental conditions, and therefore, these materials are also called intelligent or smart materials. Polymer hydrogels can be synthesized by different methods including freeze-drying [18], pyrogenation [19], microemulsion formation [20], and segment separation [21], having different geometries in the form of bead [22], film [23, 24], ring [25], and hole fiber depending on its application. Hydrogels respond to environmental stimuli, which include light [26], temperature [9, 11, 27], electric powered field [28], magnetic field [29], pH [30], ionic strength [31], chemical species [32], etc.

A number of efforts had been made within the field of hydrogels for wastewater treatment. In most studies, the researchers focus on the removal capability of hydrogels toward organic toxic dyes and inorganic toxic heavy metal ions, and nowadays, special interest is given to emergent pollutants. The distinguished emergent pollutants are pharmaceuticals, drugs, insecticides, pesticides, and other toxic chemical substances [33]. These pollutants even at very low concentrations in wastewater are highly dangerous to human bodies and aquatic animals [34].

2. Graphene oxide (GO)-based hydrogels for wastewater treatment

Polymer hydrogels are used for purification purpose, but due to weak mechanical strength, the use of these materials is restricted to some specific conditions. Therefore, to increase the application window for hydrogels, GO or some other inorganic species were introduced to fabricate composite hydrogels having enhanced mechanical strength. Besides the mechanical strength, the sheets of GO show excellent adsorption capacity for the elimination of toxic organic dyes from an aqueous environment. Currently, Guo et al. [35] carried out the facile synthesis of GO/polyethylenimine (PEI) by incorporation of GO in polyethylenimine (PEI) network producing a green adsorbent GO/PEI having enhanced removal capacity toward organic dyes. The hydrogen bonding and electrostatic interactions among amine groups of PEI and GO sheets accomplished the GO/PEI hydrogels. The removal performance was studied for both methylene blue (MB) and rhodamine B (Rhb). The as-prepared hydrogels show complete removal of these dyes within 4 h followed by the pseudo-second-order kinetics. The superior dye removal ability of hydrogels is strongly attributed to the GO sheets, while the PEI is responsible for the facilitation of the gelation process of GO sheets. The beauty of these hydrogels is that it can be recovered and reused again without any trouble from an aqueous environment, suggesting the potential importance of these materials for wastewater treatment.

Figure 1 shows the various steps occurring in the formulation of GO/PEI hydrogels. The GO sheets having large hydrophilic functional groups, e.g., carboxyl, hydroxyl, and epoxides (Figure 1A), on the surface can generate hydrogen bonds with amine groups of PEI under appropriate conditions. Consequently, PEI (Figure 1B) facilitates the gelation of GO sheets in an aqueous solution and also reveals the correct adsorption and adhesion properties. It was found that the dye adsorption capacity of the GO/PEI hydrogels increased with the amount of PEI in polymer network. It is due to the electrostatic attractions among the amine
functionalities in polymer network and the dye molecules. From these results, we can conclude that the adsorption capability of the GO/PEI hydrogels is largely attributed to PEI, and GO increases the mechanical strength. Therefore, in maximum composite substances, PEI is extensively applied as a robust chelating agent and organic intermediate. Furthermore, the GO/PEI composite hydrogel showed very stable self-assembly behaviors by using hydrogen bonding and electronic interactions, which confirmed an extraordinary possibility to launch PEI to motive secondary waste as dye adsorbents for wastewater treatment.

3. Jute/polyacrylic acid hydrogel systems for wastewater treatment

In real life the materials having high adsorption capacity, rapid removal kinetics, reusability, and cost-effective are preferred to utilize in wastewater treatment. To achieve these properties, a porous Jute/Polyacrylic acid (Jute/PAA) hydrogel was prepared. The high permeability and 80 wt% water in polymer network of Jute/PAA hydrogel made the inner sites fully available for the adsorption of metal ions. The Jute/PAA gel adsorbs heavy metal ions particularly Cd\(^{2+}\) and Pb\(^{2+}\) from wastewater with very high adsorption capacities of 401.7 and 542.9 mg/g for Cd\(^{2+}\) and Pb\(^{2+}\), respectively. Furthermore, the adsorption equilibrium was reached within 10 min for 40 mg/L of initial ion concentration using 1 g/L of hydrogel. Meanwhile, the elimination efficiencies reached 81% for Pb\(^{2+}\) and 79.3% for Cd\(^{2+}\). The materials were checked for other metal ions such as Cu, Zn, Mn, Cr, and Fe in melting wastewater under the same environmental conditions using different amount of hydrogel, and the results are tabulated in Table 1. The concentrations of Pb, Cd, and Cr reduced beneath 0.001 mg/L with the use of 4 g/L adsorbent. In the fixed-bed column experiments, the treatment quantity of melting wastewater reached 2900 BV (32.8 L) only generating 50 BV (565 ml) eluent. This study strongly helps in the development of a realistic adsorption system based on hydrogel adsorbents.
Environmental Chemistry and Recent Pollution Control Approaches

for the wastewater treatment. Therefore, the removal performance of hydrogels toward heavy metal ions was investigated in real industrial water collected from smelting plant.

The preferential removal to low degree of Fe and Cr is because of the excessive average valence electron power and the configuration of 3d^64s^2 subshell, which provides empty orbital and strongly coordination ability [36]. When increasing the adsorbent dosage to 2 g/L, Pb was preferentially removed in divalent metallic ions with the residual attention below 0.001 mg/L, probably because of the better electronegativity of Pb. While in addition to increasing the Jute/PAA gel dosage to 4 g/L, the Cd ions could be completely adsorbed, and the removal efficiencies of Cu, Zn, and Mn ions attain up to 99.8, 90.5, and 61.6%, respectively. From the obtained results, it is confirmed that the Jute/PAA hydrogel has a strong capability in the removal of heavy metal ions from commercial effluents.

Table 1 shows the adsorption statistics of heavy metal ions through different amount of Jute/PAA hydrogel dosage after remedy for 2 h.

| Sorbent dosage (g/L) | Pb (mg/L) | Cd (mg/L) | Cu (mg/L) | Zn (mg/L) | Mn (mg/L) | Cr (mg/L) | Fe (mg/L) |
|----------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 0                    | 3.825     | 6.075     | 9.325     | 188.6     | 17.05     | 0.25      | 9.75      |
| 1                    | 0.725     | 1.255     | 1.550     | 132.5     | 13.25     | <0.001    | <0.01     |
| 2                    | <0.001    | 0.225     | 0.350     | 94.65     | 11.15     | <0.001    | <0.01     |
| 3                    | <0.001    | 0.075     | 0.085     | 40.55     | 6.55      | <0.001    | <0.01     |
| 4                    | <0.001    | <0.001    | 0.010     | 17.95     | 3.05      | <0.001    | <0.01     |

Table 1. Metal ion concentrations of industrial effluent by different adsorbent dose [37].

4. Carboxymethyl cellulose/2-acrylamido-2-methyl propane sulfonic acid hydrogels

A series of functional copolymer hydrogels composed of carboxymethyl cellulose (CMC) and 2-acrylamido-2-methyl propane sulfonic acid (AMPS) have been synthesized using γ-radiations and prompted copolymerization and cross-linking, and their swelling ability was investigated to optimum conditions. The capacity of these hydrogels was tested in the recovery of toxic heavy metal ions, i.e., Mn^{2+}, Co^{2+}, Cu^{2+}, and Fe^{3+}, from their aqueous solutions. The hydrogels showed a pronounced effect on the removal of metal ions. The pronounced removal ability is due to the existence of AMPS in the inner composition of hydrogels, which has a strong chelating potential and forms a stable interaction with metal ions. Therefore, by increasing the AMPS concentration in polymer chains, the chelating potential increases, and the hydrogels will show enhanced removal performance. The prepared hydrogels of CMC/AMPS were stable and utilized in a multiple cycles with no reduction compared to their initial performance.

The adsorption process will be more active and favorable if the interaction of metal ions with the adsorbent is strong. Therefore, the effect of contact time on the adsorption ability of the CMC/AMPS copolymer hydrogel toward metal ions, i.e., Co, Mn, Cu, and Fe, changed. Initially the adsorbed amount of metal ions was efficient and then reduced. Few researchers studied and found that the decrease of chelating ability resulted in polymer chain shrinkage that takes area due to adsorption happening at the hydrogel network, due to which the diffusion of cations...
become difficult inside the bulk of the hydrogel. The fast adsorption process in the initial stage occurs on the surface and after the adsorption takes place inside the hydrogel network and slows down due to the penetration of metal ions through the pores in the hydrogel matrix. The sorption process depends on the intraparticle diffusion, chelation, and ion interactions. Table 2 shows the adsorption rate constant obtained by removing different metal ions from wastewater.

In other studies, the environment friendly carboxymethyl cellulose (CMC) hydrogel beads were successfully prepared using epichlorohydrin (ECH) as a cross-linking agent through ether linkage formed between ECH and CMC in the suspension of fluid wax. The characteristic bands in FTIR spectra confirmed the ether linkage. The prepared hydrogel beads were 4 mm in diameter with fully transparent and apparently spherical geometry. It was further confirmed by X-ray diffraction (XRD) patterns that the adsorption of metal ion onto the oxygen atom of carboxyl group changed the crystallinity of hydrogels. The adsorption capacity depends on the initial concentrations of metal ions and the pH value of metal ion solution and was found increased with increase in pH and initial concentration of metal ion solution. After the application of Freundlich and Langmuir isotherm models on the data obtained from the batch adsorption experiments, it was found that the sorption mechanism of the hydrogel beads for metal ions follows the Langmuir model. The maximum adsorption values of hydrogel beads for metal ions is 6.49, 4.06, and 5.15 mmol/g for Cu\(^{2+}\), Ni\(^{2+}\), and Pb\(^{2+}\), respectively.

Superabsorbent hydrogel beads based on CMC were prepared by suspension cross-linking method and were characterized by FTIR, XRD, and SEM. The crystallinity of these hydrogels was less than the pure CMC and was confirmed by XRD analysis. It was assumed that the adsorption of metal ions on hydrogel beads formed coordination bonds with the oxygen atoms in the carboxyl groups of hydrogel beads and showed good adsorption ability for heavy metal ions. The maximum amount of adsorbed metal ions from the data of Langmuir model is 6.49, 4.06, and 5.15 mmol/g for Cu\(^{2+}\), Ni\(^{2+}\), and Pb\(^{2+}\), respectively, at pH 7. The study of adsorption indicates that the hydrogel beads have a potential application and can be applied on large scale for wastewater treatment [39].

5. Hydrogels based on natural polysaccharides for wastewater treatment

Nowadays hydrogels based on bio-originated polymers like chitosan, maltodextrin, and gum arabic with and without magnetite nanoparticles had been employed as adsorbents for entrapping of heavy metal ions from aqueous solutions. The adsorption and removal of heavy metal ions by hydrogels are due to the diffusion of water molecules inside the hydrogel network and confirmed by adsorption kinetics using the Fickian equation. The shape of macromolecules rests and can be laid low with the presence of magnetite nanoparticles, and this effect is associated with the reticulation factors inside the hydrogel network. The CS-, M-malto-, and
M-GA-based hydrogels were applied for the removal of Cd\(^{2+}\) ions from aqueous solutions under the controlled conditions of pH 4.5–5.5, initial concentration of 20 mg L\(^{-1}\), and dried hydrogel mass of 100 mg [40]. By applying three adsorption isotherms, i.e., Langmuir, Freundlich, and Redlich-Peterson, it was found that a change in physiochemical phenomena related to Cd\(^{2+}\) adsorption occurred and the data fitted to the Langmuir or Redlich-Peterson models more than the Freundlich model. The beauty and advantage of these materials are recovery by a simple magnetic field compared to other hydrogels that require mostly ultracentrifugation or using solvents like HCl, HNO\(_3\), etc.

The removal of heavy metals from water and industrial effluents has been the goal of a large number of studies. Paulino et al. concluded from their results that hydrogels based on polysaccharides such as CS, M-malto, and M-GA are important absorbers for the treatment of wastewater and removal of heavy metal ions from industrial effluents. It was also elaborated that the diffusion of Cd\(^{2+}\) through polymer hydrogel network changed when magnetic nanoparticles were introduced into polymer network. Based on Fickian parameters, the hydrogels have diffusion properties with a tendency toward macromolecular relaxation, which is very important for adsorption studies of both organic and inorganic pollutants. Different parameters such as contact time, pH, initial hydrogel dosage, and initial concentration of the Cd\(^{2+}\) solution were studied to examine the potential application of hydrogels with and without magnetic properties for the removal of Cd\(^{2+}\) from water and effluents. The results confirmed that hydrogels without magnetic nanoparticles based only on CS, M-malto, and M-GA can be applied more efficiently in wastewater treatment for the removal of Cd\(^{2+}\) compared to hydrogels with magnetic particles. However, the regeneration of magnetic hydrogels can be done more easily with the application of magnetic field which is environmental friendly and green approach [40].

6. Treatment of polluted water resources using reactive polymeric hydrogel

An experimental work becomes performed to study the overall performance of the prepared polyvinyl pyrrolidone/acrylic acid (PVP/AAc) copolymer hydrogel to chelate heavy metals from the bulk material [41]. The results clearly indicate that PVP/AAc copolymer hydrogel has excessive binding capacities and proper adsorption kinetics for the metal ions. The sorption of these metal ions follows the Langmuir adsorption isotherm. The feasibility for the uses of PVP/AAc hydrogel for the treatment of polluted samples, accrued from distinct water assets in Helwan location (Egypt), was investigated. The results showed that by using these hydrogels, we can obtain pure usable water from wastewater.

In recent years, there has been considerable interest in the chelation of metal ions by insoluble cross-linked polymeric substrate. Such substrates have advantages over soluble materials of easy separation from the reaction medium, leading to operational flexibility of their facial regenerability and of higher stability. The removal performance of hydrogels can be disturbed in the presence of other metal salts like NaCl, MgCl\(_2\), CaCl\(_2\), etc. in polluted water and affect the chelating ability of the species. This effect was studied by Shawky et al. in the adsorption of Fe ions by PVP/AAc hydrogel in the presence of different metal salts, and the effect is shown in Figure 2. No effect on the adsorption of Fe ions was observed in case of NaCl even at high concentration of NaCl. Furthermore, Fe adsorption is not suffering by low concentrations of CaCl\(_2\) and MgCl\(_2\); however, at higher concentrations, the adsorption decreases, and this could be attributed to the affinity of the reactive polymers toward alkaline earth metals as compared to transition metal ions.
The results obtained clearly demonstrate and confirmed the applicability of PVP/AAc hydrogel for wastewater treatment. Water resources in the Helwan area showed that trace metal contents are very high when the analysis of nine water samples was carried out. The hydrogel treatment resulted in a satisfactory removal of polluted heavy metals especially iron, manganese, and aluminum [41].

7. Conclusion

The smart polymer hydrogels prepared from both synthetic and natural polymers can be used successfully with full confidence for wastewater treatment. However, the properties of these hydrogels will be kept according to the required environmental conditions by changing the composition of polymer networks. The performance of few polymer hydrogels was explained and executed in this chapter, which clearly indicates that due to smart behavior, easy synthesis, recycling, low cost, environment friendly, biocompatibility, etc. make these hydrogels as efficient candidate compared to other materials for wastewater treatment. By reading this chapter, the researchers could find new approaches which help them in designing new hydrogel systems for different applications.

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References

[1] Fu F, Wang Q. Removal of heavy metal ions from wastewaters: A review. Journal of Environmental Management. 2011;92(3):407-418

[2] Charerntanyarak L. Heavy metals removal by chemical coagulation and precipitation. Water Science and Technology. 1999;39(10-11):135-138

[3] Wang M et al. Hybrid algal photosynthesis and ion exchange (HAPIX) process for high ammonium strength wastewater treatment. Water Research. 2018;142:65-74

[4] Vashi H, Iorhemen OT, Tay JH. Aerobic granulation: A recent development on the biological treatment of pulp and paper wastewater. Environmental Technology and Innovation. 2018;9:265-274

[5] Cui X et al. Dark matter results from 54-ton-day exposure of PandaX-II experiment. Physical Review Letters. 2017;119(18):181302

[6] Volpin F et al. Simultaneous phosphorous and nitrogen recovery from source-separated urine: A novel application for fertiliser drawn forward osmosis. Chemosphere. 2018;203:482-489

[7] Choumane FZ et al. Valorisation of a bioflocculant and hydroxyapatites as coagulation-flocculation adjuvants in wastewater treatment of the steppe in the wilaya of Saida (Algeria). Ecological Engineering. 2017;107:152-159

[8] Shah LA et al. Synthesis of sensitive hybrid polymer microgels for catalytic reduction of organic pollutants. Journal of Environmental Chemical Engineering. 2016;4(3):3492-3497

[9] Shah LA et al. Thermal and pH dual responsive copolymer and silver nanoparticle composite for catalytic application. Chinese Journal of Chemistry. 2015;33(4):467-472

[10] Shah LA et al. Silver nanoparticles fabricated hybrid microgels for optical and catalytic study. Journal of the Chemical Society of Pakistan. 2016;38(5):850-858

[11] Shah LA et al. Ag-loaded thermo-sensitive composite microgels for enhanced catalytic reduction of methylene blue. Nanotechnology for Environmental Engineering. 2017;2(1):14

[12] Shah LA et al. TiO$_2$ nanotubes doped poly (vinylidene fluoride) polymer membranes (PVDF/TNT) for efficient photocatalytic degradation of brilliant green dye. Journal of Environmental Chemical Engineering. 2019;7:103291

[13] Javed R et al. Uptake of heavy metal ions from aqueous media by hydrogels and their conversion to nanoparticles for generation of a catalyst system: Two-fold application study. RSC Advances. 2018;8(27):14787-14797

[14] Li J et al. Metal–organic framework-based materials: Superior adsorbents for the capture of toxic and radioactive metal ions. Chemical Society Reviews. 2018;47(7):2322-2356

[15] Rehman TU et al. Zwitterionic superabsorbent polymer hydrogels for efficient and selective removal of organic dyes. RSC Advances. 2019;9(32):18565-18577

[16] Shah LA. Developing Ag-tercopolymer microgels for the catalytic reduction of p-nitrophenol and EosinY throughout the entire pH range. Journal of Molecular Liquids. 2019;288:11045

[17] Cruz H et al. Rapid removal of ammonium from domestic wastewater
using polymer hydrogels. Scientific Reports. 2018;8(1):2912

[18] Butylina S, Geng S, Oksman K. Properties of as-prepared and freeze-dried hydrogels made from poly (vinyl alcohol) and cellulose nanocrystals using freeze-thaw technique. European Polymer Journal. 2016;81:386-396

[19] Badiger MV, McNeill ME, Graham NB. Porogens in the preparation of microporous hydrogels based on poly (ethylene oxides). Biomaterials. 1993;14(14):1059-1063

[20] Ghayempour S, Montazer M. A modified microemulsion method for fabrication of hydrogel Tragacanth nanofibers. International Journal of Biological Macromolecules. 2018;115:317-323

[21] Omidian H, Rocca JG, Park K. Advances in superporous hydrogels. Journal of Controlled Release. 2005;102(1):3-12

[22] Farhoudian S, Yadollahi M, Namazi H. Facile synthesis of antibacterial chitosan/CuO bio-nanocomposite hydrogel beads. International Journal of Biological Macromolecules. 2016;82:837-843

[23] Zhang W et al. A family of metal-organic frameworks exhibiting size-selective catalysis with encapsulated noble-metal nanoparticles. Advanced Materials. 2014;26(24):4056-4060

[24] Zhang M, Zhang Y, Helleur R. Selective adsorption of Ag+ by ion-imprinted O-carboxymethyl chitosan beads grafted with thiourea–glutaraldehyde. Chemical Engineering Journal. 2015;264:56-65

[25] Deng Y et al. Insight into highly efficient simultaneous photocatalytic removal of Cr (VI) and 2, 4-dichlorophenol under visible light irradiation by phosphorus doped porous ultrathin g-C3N4 nanosheets from aqueous media: Performance and reaction mechanism. Applied Catalysis B: Environmental. 2017;203:343-354

[26] Tomatsu I, Peng K, Kros A. Photoresponsive hydrogels for biomedical applications. Advanced Drug Delivery Reviews. 2011;63(14-15):1257-1266

[27] Shah LA, Sayed M, Siddiq M. Fabrication of Ag and Au nanoparticles in cross-linked polymer microgels for their comparative catalytic study. Materials Science-Poland. 2017;35(3):651-659

[28] Kim SJ et al. Behavior in electric fields of smart hydrogels with potential application as bio-inspired actuators. Smart Materials and Structures. 2005;14(4):511

[29] Liu TY et al. Magnetic-sensitive behavior of intelligent ferrogels for controlled release of drug. Langmuir. 2006;22(14):5974-5978

[30] Rogina A et al. Cellular hydrogels based on pH-responsive chitosan-hydroxyapatite system. Carbohydrate Polymers. 2017;166:173-182

[31] Zhang R et al. A novel pH-and ionic-strength-sensitive carboxy methyl dextran hydrogel. Biomaterials. 2005;26(22):4677-4683

[32] Yoshida R, Okano T. Stimuli-responsive hydrogels and their application to functional materials. In: Biomedical Applications of Hydrogels Handbook. New York, Dordrecht, Heidelberg, London: Springer; 2010. pp. 19-43

[33] Geissen V et al. Emerging pollutants in the environment: A challenge for water resource management. International Soil and Water Conservation Research. 2015;3(1):57-65
[34] Pakdel PM, Peighambardoust SJ. Review on recent progress in chitosan-based hydrogels for wastewater treatment application. Carbohydrate Polymers. 2018;201:264-279

[35] Guo H et al. Preparation of graphene oxide-based hydrogels as efficient dye adsorbents for wastewater treatment. Nanoscale Research Letters. 2015;10(1):272

[36] Berlia R, Kumar MP, Srivastava C. Electrochemical behavior of Sn–graphene composite coating. RSC Advances. 2015;5(87):71413-71418

[37] Zhou G et al. Efficient heavy metal removal from industrial melting effluent using fixed-bed process based on porous hydrogel adsorbents. Water Research. 2018;131:246-254

[38] Ahmed S et al. Advances in heterogeneous photocatalytic degradation of phenols and dyes in wastewater: A review. Water, Air, and Soil Pollution. 2011;215(1-4):3-29

[39] Yang S et al. Hydrogel beads based on carboxymethyl cellulose for removal heavy metal ions. Journal of Applied Polymer Science. 2011;119(2):1204-1210

[40] Paulino AT et al. Efficiency of hydrogels based on natural polysaccharides in the removal of Cd\(^{2+}\) ions from aqueous solutions. Chemical Engineering Journal. 2011;168(1):68-76

[41] Shawky H et al. Treatment of polluted water resources using reactive polymeric hydrogel. Journal of Applied Polymer Science. 2006;100(5):3966-3973