Microchemical Journal 168 (2021) 106357

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Eco-friendly polyacrylic acid based porous hydrogel for heavy metal ions adsorption: characterization, adsorption behavior, thermodynamic and reusability studies

F.O. Gokmen [*], E. Yaman, S. Temel

Central Research Laboratory, Bilecik Seyh Edebali University, Bilecik, Turkey

ARTICLE INFO

Keywords:
Poly (acrylic acid) hydrogel
Re-usability
Heavy metal ions
Adsorption
Swelling behaviour
Waste-water treatment

ABSTRACT

Hydrogels are the most commonly used 3D polymer mesh materials for environmental removal due to their ability to hold water in their porous structures. In this study, polymeric hydrogels were used for metal removal from wastewater. Polyacrylic acid is an environmentally friendly polymer with known biodegradable and antimicrobial properties. Polyacrylic acid based (PAA) hydrogel were used as an adsorbent for removal of the M^{2+} (Cd^{2+}, Ni^{2+} and Cu^{2+}) and Fe^{3+} ions from aqueous solutions in this study. Eco-friendly functional PAA-based hydrogel was obtained by in-situ free radical polymerization technique. The effect of pH on the swelling characteristic of hydrogel was examined exhaustively and the highest swelling capacity as 1200% was seen for 2% cross-linked PAA hydrogel at pH 10. All these samples gave highly impressive results in the adsorption of Cu^{2+}, Cd^{2+}, Ni^{2+}, and Fe^{3+} from water solutions at pH values between 2 and 10. The highest adsorption capacity of the metal ions on hydrogel was specified as Cd^{2+} ion. Due to its clean production process, high heavy-metal adsorption capacity and the re-usability, PAA-based hydrogels have a high potential as an eco-friendly cleaner production material.

1. Introduction

Polymeric hydrogels can retain multiple layers of water in their structures [1–3]. Hydrogels due to their extremely superior water retention properties; show hydrophilic character and high swelling behaviour, also they are biocompatible and can be obtained in desired large masses [4]. A 3D cross-linked system using hydrophilic polymers, referred as hydrogels, which swells and absorbs water onto their structure to swell in solutions. Hydrogels are most attractive materials of “soft matter” preferred in various application areas [5]. Hydrogels can be used in many systems; agriculture and botanic [6], drug delivery systems [7], medical systems [8], tissue engineering [9], protein and cell immobilization [10], wastewater treatment [11]. Nowadays, there has been a marked strength in the improvement of the hydrogel composite and their application in several purposes, contain environmental improvement [12–14]. Concerning contaminated water, hydrogel based composites have shown upper performance in adsorption of different inorganic and organic pollutants [15,16]. Hydrogel based composites are adapted to cover most applications to achieve more functional properties such as greatest balance swelling, higher absorption rate, small residue content, porosity, smooth softness, high strength, odourless, photo stability [17].

With the rapid increase in the global population and the need for continuous industrialization, the pollution problem that is at the basis of life, such as clean water, is the foremost threat. As a basic result of this problem, the loss of 6 children per minute reveals the importance of studies in this area [18]. Heavy metals, the most common water pollutants, cause serious adverse health effects. Since heavy metals cannot be degraded by natural biological means, the water treatment industry has been working to find solutions for decades [19,20]. Water is the basic necessity of all life in nature. The development of chemical industry and extensive application of many chemical agents in agriculture, harmful compounds have been polluted air and soil, and consequently, drinking water, which resulted in numerous diseases. Heavy metal ions become serious threats to ecological environment due to not biodegradable and tend to accumulate in living tissues [21]. Economically, hydrogels are the most suitable materials for waste water removal. Because of the adsorption limits do not decrease after several recovery and reuse [22]. Having high adsorption limit, mechanical strength, biodegradability and reusability in various pH ranges all make sense of

---

[*] Corresponding author.
E-mail addresses: fatmaozge.gokmen@bilecik.edu.tr (F.O. Gokmen), elif.yaman@bilecik.edu.tr (E. Yaman), sinan.temel@bilecik.edu.tr (S. Temel).

https://doi.org/10.1016/j.microc.2021.106357
Received 1 March 2021; Received in revised form 6 April 2021; Accepted 7 April 2021

hydrogels in removing all impurities from wastewater [22]. To improve the quality of life, polymer material is widely used due to its durability, density and cost-effective nature. Hydrophilic structure of hydrogels is due to the number of polar hydrophilic groups like –OH, –COOH, –$CONH_2$ and –SO_3H. These groups are attached onto polymer chain with response to different stimuli [23]. Hydrogel has been found to exhibit incredibly extraordinary properties for reusability. Previous studies have shown that up to five adsorption–desorption cycle hydrogels give good results [24]. In the wastewater treatment applications, reusability is the most important property for an adsorbent [17,25]. In adsorption applications where harmful particles are immobilized on a substrate and contributes to the improvement of dispersion, the adsorption capacity of the substrate can be increased by improving the surface properties. Particles immobilized on the substrate by adsorption play an active role in most cases, depending on the degree of exposure and contact between the pollutants and the adsorbent [26]. A wide variety of physical and chemical treatment processes are used to treat wastewater and contaminated water. The mechanisms used make use of either the pore size differences or the chemical affinity between the substrate and the pollutant. These two mechanisms can work separately or simultaneously in the adsorption process [27].

Since heavy metals directly and indirectly cause health problems in contact with people and aquatic animals, it is significant to remove these ions from wastewater [28]. Heavy metals accumulate easily in the human body, causing serious illnesses ranging from liver damage to kidney failure and also affect food chain directly. For this reason, specific guidelines for water quality components, including heavy metal ions, are reported by the World Health Organization with up-to-date revisions [19,20,29]. For example, the Cd ion accumulated and retained in the body is a toxic heavy metal that causes bone and lung cancer and kidney damage to occur [30]. The well known "Itai-Itai disease" is a typical case of chronic cadmium poisoning [20]. Similarly, large amounts of Ni cause serious effects on the human body such as lung embolism, heart conditions, respiratory failure and birth defects [31]. Excess cupper ion in humans causes diarrhea, nausea, dizziness and headache [32]. In addition, excess of ionic iron (Fe^{2+} and Fe^{3+}) in water is toxic to aquatic life and it can be caused deadly effect on them [33]. Although these metals have toxic affect for the humans and the environment in high concentrations, usage of these metals is also crucial for numerous routine processes [34]. Therefore, it is necessary to adopt an easy and effective technique for removing heavy metal ions from wastewater [35]. Today, some methods have been designed to remove toxic inorganic ions from contaminated water such as electrochemical treatment, ion exchange resins, ultrafiltration nozzles etc. Among these techniques, adsorption based processes are extensively used to remove metal ions from wastewater owing to its low operating costs, higher efficiency, simple of use and lower sludge production [36]. Adsorption has been recognized as an easy-to-apply technique for removing contaminants from contaminated environments. The porous structure of the adsorbents facilitates this process. For the adsorption mechanism using various adsorbents, adjustable pore structure and high surface area/mass ratio with chemical stability are the most important factors [29]. In their study, Alharbi et al. summarized the advantages and disadvantages of different methods in removing pollutants in the form as a table [19]. Adsorption technology is a purification technique that utilizes the high adsorption capacity of adsorbents to remove certain contaminants. The most general properties required from a good adsorbent; large specific surface area, high adsorption performance, outstanding selectivity, excellent chemical and thermal stability, cheap availability and reusability. Adsorption is affected by the physical and chemical properties of pollutants, pH values, coexisting substances, temperature, contact time and adsorbent dosage. As reported in previous studies, adsorption mechanisms occur through ion exchange, electrostatic adsorption, hydrogen bonding, specific surface bonding, and chelation [20].

In 2018, Du et., al synthesized hydrogels via by using in-situ polymerization technique of acrylic acid (AA) in PVA solution, and poly (acrylic acid) (PAA) chains were cross-linked with N,N′-methylene bis-(2-propenamide) (MBA). They chose PAA for its high Tg degree and SiC for higher temperature stability [37]. In this work PAA-based hydrogel was synthesized by in situ radical polymerization technique. The obtained hydrogels were characterized by morphological (Field Emission Scanning Electron Microscopy) and structural (Fourier Transform Infrared Spectroscopy). The characterized hydrogel was used for the removal of Cu^{2+}, Ni^{2+}, Cd^{2+} and Fe^{3+} heavy metal ions from aqueous solutions in different ranges of concentrations, temperatures and pH. The adsorption capacities of prepared with variety range of concentration metal ion aqueous solutions samples were determined using by Atomic Absorption Spectroscopy (AAS). Adsorption isotherms, adsorption kinetics and adsorption thermodynamics have been studied in detail.

2. Experimental

2.1. Chemicals and reagents

Materials used throughout this study; acrylic acid, ammonium persulfate, N,N′-methylenebisacrylamide (N,N′-MBAAm) were purchased from Sigma-Aldrich, USA. Copper(II) acetate monohydrate, nickel(II) nitrate hexahydrate and cadmium acetate dihydrate, iron(III) nitrate nonahdrate were supplied from Merck, Germany and Sigma Aldrich, USA, respectively. For pH adjustment NaOH, NH_4OH and HCl were used from Merck, Germany. Deionized water was used in all experimental stages.

2.2. Synthesis of poly (acrylic acid) based hydrogels

Free radical polymerization technique used to synthesize acrylic acid (AA) hydrogel by using with a radicalic initiator (ammonium persulfate) and a crosslinking agent (N,N′ methylenebis(acrylamide)). The hydrogel solution was prepared presence of monomer (5.5 mol L^{-1}), initiator (0.01 mol L^{-1}) and crosslinking agent (0.45 mol L^{-1}) in deionized water. All chemicals were filled into PVC straws, heated in a water bath to 80 °C and waited this temperature for 2 h. Then, hydrogel was carefully released from the PVC straws. The obtained hydrogel samples were cut in cylindrical shape (3–4 mm in length) equally, and the hydrogels were dried in a room condition for overnight.

2.3. Characterization of PAA-hydrogel

2.3.1. Swelling behaviour

The swelling behaviour of PAA-based hydrogel was followed 56 h in water at room temperature at different pH range (2–10). Each part of the dried and weighed hydrogel samples was placed in 10 mL of distilled water. At each time point, the scaffolds were taken out of the water solution and were weighed at steady time intervals after removing the excess water until equilibrium was reached. The swelling ratio (S, %) was determined among the equation is given below;

$$Swelling, \% = \frac{m_t - m_1}{m_1} \times 100 \tag{1}$$

where m_t is mass of swelling at time t and m_1 is mass of hydrogel used as adsorbents

2.3.2. FT-IR spectroscopy

The chemical structure of PAA hydrogels obtained from acrylic acid monomer with radical polymerization technique has been proven with FT-IR analysis by Perkin Elmer, USA, Spectrum 100 model FT-IR. The wavelength is in the range of 400–4000 cm^{-1}. Attenuated Total Reflection (ATR) module was used and each spectrum was scanned 4 times and studied at a resolution of 4 cm^{-1}.

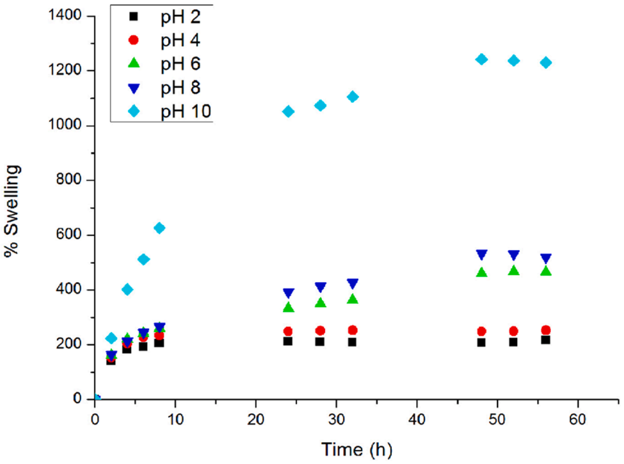

Fig. 1. Swelling behaviour of PAA-based hydrogel in the range of pH 2–10 at 56 h.

2.3.3. *SEM-EDX and elemental mapping analysis*

FESEM analyses were recorded with Carl Zeiss, Germany, Supra 40VP model SEM. Metal ion dispersion in PAA hydrogel were scanned by carrying out the mapping technique with the Bruker EDX detector. In order to confirm the results of metal ions adsorption and desorption, EDX analysis was conducted on samples.

2.3.4. *Batch adsorption studies*

The analytical grade salts copper(II) acetate monohydrate, nickel(II) nitrate hexahydrate and cadmium acetate dehydrate, iron(III) nitrate nonahydrate procured were utilized to prepare a stock solution of 1000 ppm. 50, 100, 150, 200 and 250 ppm solutions were prepared by diluting the 1000 ppm stock solution.

The batch adsorption studies were accomplished in a 50 mL flask each were contained 10 mL of salt solution except the cases where the initial metal ion concentration and temperature were varied. The concentration of the metal solutions was measured before and after the adsorption studies using Atomic Absorption Spectrophotometer (AAS) (Perkin Elmer, USA, Elmer Analyst 800). In this study, initial metal concentration and temperature affect were examined as the parameters on the adsorption of Cu^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+}. The quantity of metal adsorbed onto per gram of adsorbent (q_e) and the percentage removal efficiency (% Removal) were determined by using Eqs. (2) and (3), respectively [38].

$$q_e = \frac{V(C_o - C_e)}{m} \tag{2}$$

$$\%\text{Removal} = \frac{C_o - C_e}{C_o} \times 100 \tag{3}$$

Table 1
FT-IR functional groups of PAA-based hydrogel.

Functional groups	Wave number (cm^{-1})
—OH	3500–3300
C—H	2935
—C=O	1693
—C—O	1238, 1161

In this equation, C_o is initial metal concentration (mg/L), C_e is metal concentration in equilibrium (mg/L), V is the metal solution volume (L) and m is the adsorbent mass (g).

2.3.5. *Batch desorption studies*

The desorption of Cu^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} studies were performed using batch experiments with pH 2 solution, waiting for 48 h to equilibrate on desorption. Initial metal concentration and volume of the solution were kept fixed at 250 ppm and 10 mL, respectively. At the end of the equilibration time, the sorbent was separated and the supernatant was exposed to the measurement of residual metal ion density. The concentration of the metal solutions was measured before and after the desorption experiments using AAS. The percentage of desorption (Desorption %) was determined using Eq. (4):

$$Desorption, \% = \frac{C_o}{C_e} \times 100 \tag{4}$$

In this equation, C_0 and C_e are metal ion solution concentrations in the initial and equilibrium (ppm).

3. Results and discussion

3.1. *pH effect of swelling behaviour*

Fig. 1 shows the swelling behaviour of the hydrogel according to the pH effects. In this study, it was seen that each hydrogel sample holds a large amount of water. In each sample, the swelling value obtained after 2 h is over 120%. In the data obtained after 24 h, this value exceeded 200%. Swelling amounts of the samples increased over time and remained stable after reaching equilibrium. The increase of pH of the aqueous solutions in PAA-based hydrogel leads to a significantly change in the swelling ratio. The swelling values of hydrogel reached equilibrium in 48 h. The pH value with the highest swelling behaviour was obtained as pH 10. In solutions after pH 10, the physical structure of the gels began to deteriorate. After reaching equilibrium, the swelling size of hydrogels at different pH is given in Fig. 2. Accordingly, with the diameter of 15 mm, the largest hydrogel, which swells without being deformed, was observed at pH 10.

3.2. *FT-IR spectroscopy results*

The FT-IR results of samples before the adsorption of metal ions in hydrogels were given in Table 1. As seen in Table 1, the FT-IR spectra of

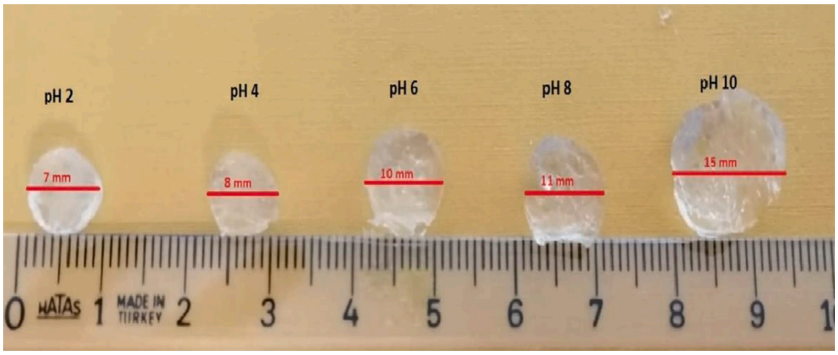

Fig. 2. Swelling sizes of PAA hydrogel at different pH (2–10).

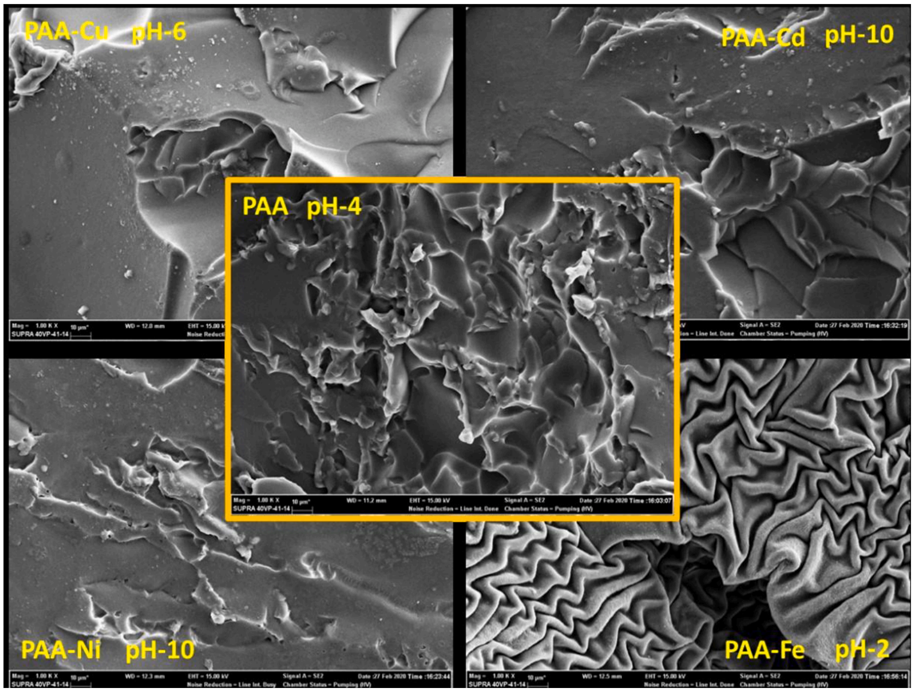

Fig. 3. The pH effect of non-adsorbed (center) and metal adsorbed hydrogel's surface SEM images (1 kX).

PAA-based hydrogel presented numerous characteristic peaks arisen from the functional groups of PAA molecules. The broad peaks within the range of 3500 to 3300 cm^{-1} can be attributed to the stretching vibrations of hydroxyl groups (—OH) in hydrogel. The peaks observed at 2935 cm^{-1} were related to the asymmetrical vibration of $—CH_2$ in PAA hydrogel [39]. The peak located at 1693 cm^{-1} induces from the stretching vibration of —C═O bands in —COOH groups [40]. The peaks around 1000–1300 cm^{-1} regions are match to the stretching vibration of —C—O bond in —COOH groups. The FT-IR results obtained for PAA are similar to the previous results of this research group [41].

3.3. Morphology of polyacrylic acid based hydrogel

Fig. 3 presents the SEM pictures of the PAA-hydrogel (placed at center) before and after the adsorption of Cu, Cd, Ni and Fe. Highly porous surface was observed for hydrogels before metals adsorption. Due to the metals engaged the active sites in the hydrogels, the surfaces were seen tight and rough.

Images were taken at 1 kX magnification. The changes in the surface morphology of hydrogel which were stabilized after 48 h in 250 ppm metal solutions at different pH are quite strong evident. Accordingly, the pH increased from 2 to 10 while the surface roughness decreased. At the lowest pH that metal adsorbed hydrogel is PAA-Fe. The surface of the PAA-Fe hydrogel is completely composed of channel lines. For this reason, the higher surface area was mostly seen in the hydrogel that adsorbed Fe ion at pH 2.

The hydrogels were classified as macroporous materials [42]. Since porosity enables interaction between molecules, it increases the adsorption capacity. Rough surfaces in hydrogels are proof of metal adsorption. This was proven by the EDX spectrum and elemental mapping of the hydrogel surfaces (Table 3 and Fig. 9).

3.4. Adsorption studies

3.4.1. Effect of initial metal concentration on removal efficiency

The adsorption of Cu^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} onto PAA-hydrogel surface was specified with a varied in the initial metal concentration from 50 to 250 ppm. The process temperature was kept fixed at room temperature, while the adsorbent dosage was about 60 mg. pH of the Cu^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} metal solutions were 6, 10, 10 and 2, respectively. Fig. 4 shows the % removal of the metals onto PAA-hydrogel as a function of the initial metal concentration. When the initial concentration increased, each metal adsorption process showed the same tendency in the percentage removal increased. By the reasons of the saturation of the adsorption active centers on the adsorbent surface, no significant change in adsorption was observed after 150 ppm. While the maximum % removal was determined as 95.33% in Cd^{2+} solution where the metal concentration was 150 ppm, the minimum % removal was specified as 32.0% in Fe^{3+} solution where the metal concentration was 50 ppm. While concentration effect is not observed in Cd and Ni removal, in Fe and Cu removal percentage increased as metal concentration increased. In this study, the possible adsorption mechanism is given as follows.

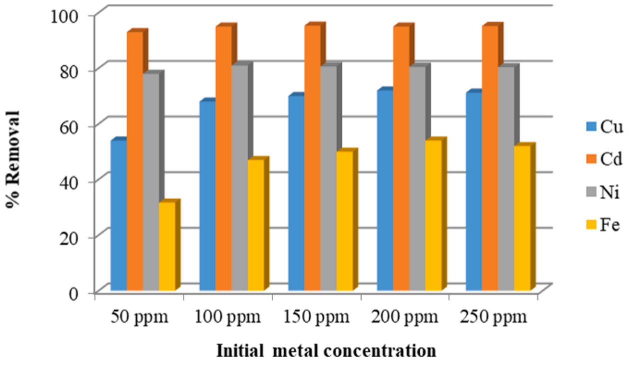

Fig. 4. Effect of initial metal concentration on % removal.

$$\sim COOH \rightarrow \sim COO^- + H^+ \tag{5}$$

$$\sim COO^- + M^{2+} \rightarrow \sim[\sim COO^-]_2\,[M]^{2+} \tag{6}$$

$$\sim COO^- + Fe^{3+} \rightarrow \sim\sim COO^-\,Fe^{3+} \tag{7}$$

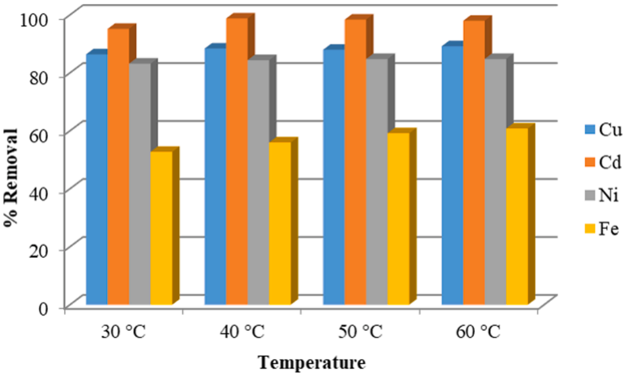

Fig. 5. Effect of temperature on % removal.

M^{2+} (Cu^{2+}, Ni^{2+} and Cd^{2+}) ions and Fe^{3+} have been adsorbed onto the surface of PAA hydrogels are assumed to occur through ion-exchange and chelating between positively charged M^{2+}; Fe^{3+} and nonionized or ionized carboxylic groups within the polymer chain of polyacrylic acid. The adsorption mechanism can be verified by the balance of adsorption provided by the pH change of the heavy metal aqueous solution formed. Hydrogels are 3D cross-linked polymer networks and have a large number of functional groups that can be used as adsorption sites in the form of ion-exchange and chelation. PAA also contains active —COOH regions. In an aqueous solution, these —COOH groups in hydrogels dissociate to give protons at which pH will drop in that solutions [43,44].

pH plays a fundamental role in the adsorption of metal ions on polymer hydrogels. Previous studies have examined the effect of pH on the swelling behavior of hydrogels. Different behaviors with changing pH were observed in this effect [45]. The swelling behavior of PAA hydrogel at pH 4 coincides with the pKa value of acrylic acid [44]. This behavior occurs at pH values higher than the pKa value of acrylic acid, the decomposition of carboxyl groups leads to the formation of carboxylate [44].

3.4.2. Effect of temperature on removal efficiency

For adsorption itself, temperature acts as a marker in exothermic and endothermic definitions. Operation temperature is also important for process feasibility and economy. The effect of temperature on the % removal was specified by the adsorption studies of Cu^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} onto PAA-hydrogel surface with a variation in the temperature from 30 to 60 °C. The initial metal concentration was kept fixed at 250 ppm. pH of the Cu^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} metal solutions were 5, 10, 10 and 3, respectively.

The results of the % removal for each temperature were given in Fig. 5. The removal efficiency of Cu^{2+}, $Cd^{2+}$and Ni^{2+} were slightly rising by increasing the temperature from 30 to 60 °C. Fe^{3+} adsorption process was the most affected process by temperature. The fact that the highest ΔH° value among other metal ions belongs to iron is a proof of this. It can be said that the increasing of the temperature has slightly effect on adsorption capacity that makes the adsorption process economical.

3.5. Adsorption isotherms

Adsorption isotherm is significant to predict behavior of solid–liquid adsorption process and the optimum efficiency of the adsorbent. It is considerable to prove the most suitable correlation for the equilibrium curves to optimize the design of the adsorption of the adsorbates [46,47]. The metal ion concentration is related to the quantity of metal ion adsorbed on the hydrogel surface used as an adsorbent. In this study, Langmuir, Freundlich and Temkin isotherm were used to specify the adsorption behavior of Cu^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} metals onto PAA-hydrogel.

3.5.1. Langmuir

The Langmuir isotherm model is the furthest used isotherm for the adsorption between liquid and solid [48]. This isotherm theory makes any assumptions: adsorption occur at significant homogenous sites therein the adsorbent, the interaction between adsorbed materials can be neglectable, and the adsorption occurs as monolayer adsorption [38]. Linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{Ce}{q_m} \tag{8}$$

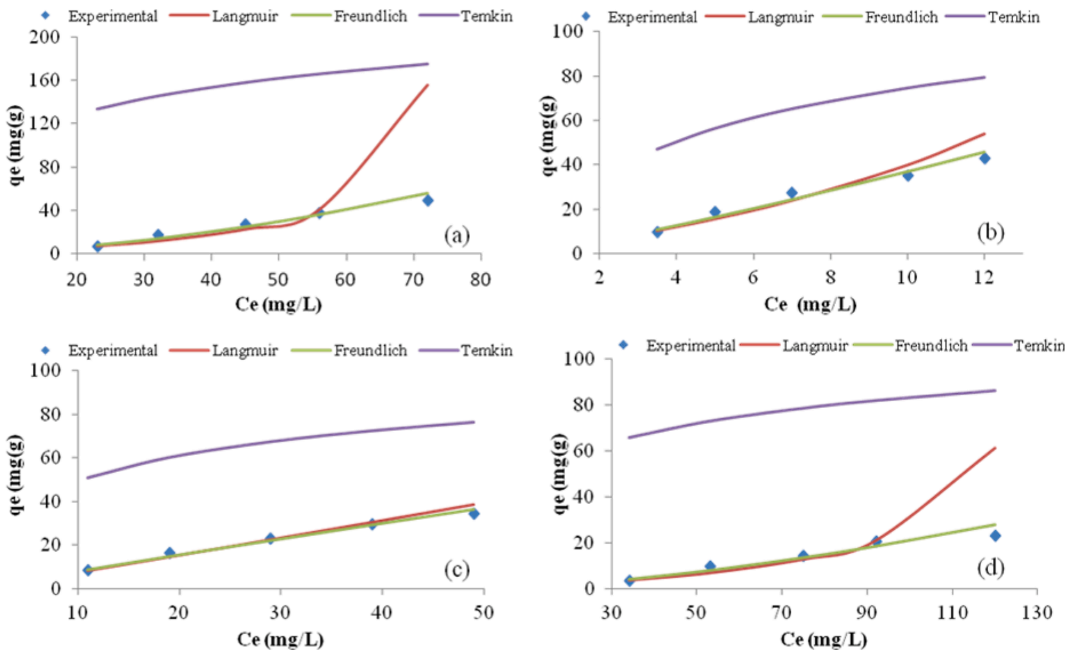

Fig. 6. Comparison of the experimental and predicted isotherm models for (a) Cu^{2+} (b) Cd^{2+} (c) Ni^{2+} (d) Fe^{3+}

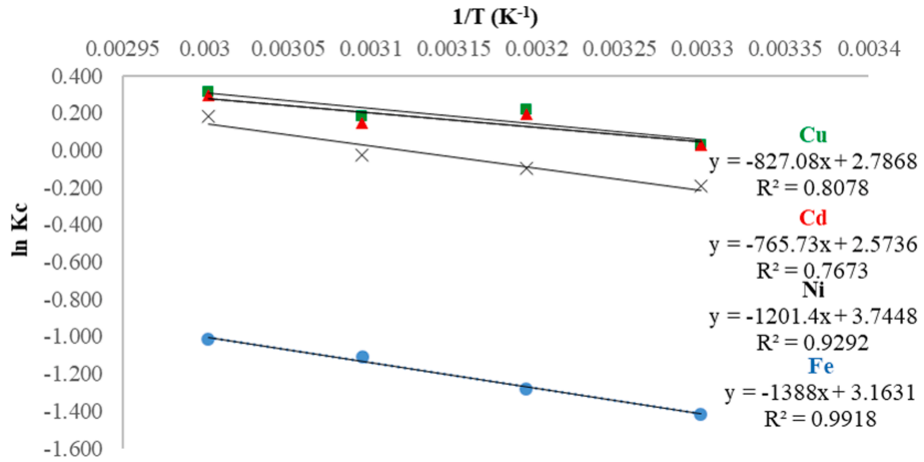

Fig. 7. Van't Hoff Plot for the adsorption of Cu, Cd, Ni and Fe onto AA hydrogel.

where q_m is the maximum adsorption capacity per unit weight adsorbent theoretically (mg/g), K_L is Langmuir constant (L/mg), C_e is the concentration of the solution at equilibrium (mg/L) and q_e is the adsorption capacity per unit weight adsorbent at equilibrium (mg/g) [49].

3.5.2. Freundlich

The Freundlich isotherm model is used to identify the heterogeneous surface with the irregular adsorption heat distribution on the adsorbate surface [50]. The linear form of Freundlich isotherm equation is given as:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{9}$$

in this equation, K_F (mg/g) and $1/n$ is Freundlich constants and C_e is the equilibrium concentration of the solution (mg/L) and q_e is the equilibrium adsorption capacity per unit weight adsorbent (mg/g) [51].

3.5.3. Temkin

The Temkin equation says that as all the degrees of the attachment centers of an adsorbent increase, the sorption energy decreases linearly. In this case, as the liquid–solid interactions rise, the adsorption heat will decrease linearly. The linear form of Temkin isotherm equation is given as:

$$q_e = B_1 lnK_T + B_1 \ln C_e \tag{10}$$

in this equation, $B_1 = RT/b$, K_T is the equilibrium binding constant (L/mg) indicating to the maximum binding energy and constant B_1 is related to the adsorption heat [47].

On the analysis of each isotherm model, it is proven from Fig. 6 the adsorption phenomena on PAA-hydrogel was not different from metal to metal. The equilibrium data were well fitted by Freundlich isotherm model for the all metal ions, so that the Freundlich isotherm was suitable model to explain the behavior of Cu^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} adsorbed onto PAA- based hydrogel. It suggests that the adsorption process had in irregular distribution of adsorption heat over the surface with heterogeneous surface.

3.6. Thermodynamic analysis

Thermodynamic analysis is important to evaluate the feasibility of the adsorption reactions which provides information about the inherent energy and structural changes [52]. In the study, the temperature range was varied from 30 to 60 °C to calculate thermodynamic parameters such as: standard free energy change △G (kJ/mol), standard enthalpy change △H (kJ/mol) and standard entropy change △S (kJ/mol.K). Therefore, △H and △S were determined from the Van't Hoff equation as follow:

$$lnK_c = \frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{11}$$

Table 2
Thermodynamic parameters of Cu, Cd, Ni and Fe adsorption onto AA hydrogel.

	ΔG° (kJ/mol)				ΔH° (kJ/mol)	ΔS° (kJ/mol.K)
	30 °C	40 °C	50 °C	60 °C		
Cu	−0.074	−0.558	−0.482	−0.867	6.876	23.170
Cd	−0.061	−0.504	−0.387	−0.812	6.366	21.397
Ni	0.492	0.261	0.076	−0.499	9.988	31.134
Fe	3.568	3.334	2.980	2.811	11.540	26.298

The relationship between △G and K_c is given in Eq. (12). Here, *T (K)* is the temperature and R (8.314 J/mol2K) is the gas constant [53]:

$$\Delta G = -RTln(K_c) \tag{12}$$

According to thermodynamic analysis, Van't Hoff Plot for the adsorption of Cu^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} onto AA hydrogel were given in Fig. 7. The thermodynamic parameters of ΔG° (kJ/mol), ΔH° (kJ/mol) and ΔS° (kJ/mol·K) of adsorption obtained for the Cu^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} adsorption were also given in Table 2. The negative slope in the Van't Hoff equation and the positive ΔH° values found for each metal ions in adsorption indicate that the adsorption process is endothermic. We can also say that the metal ion adsorption on the PAA hydrogel is endothermic, showing that ion uptake increases as the temperature increases. The values of ΔH° are within the 1–93 kJ/mol demonstrate that the adsorption mechanism is physisorption [51]. From Table 2, it is seen that physisorption is more sufficient for all the metal ions adsorption process. The positive values of ΔS prove an overall entropy increase for the adsorption, which is referred to the increase in the randomness at the liquid–solid interface during adsorption [38]. This randomness increases with the ion activity and water molecules while dehydration or the replacement of a larger amount of species obtained from the adsorbent surface with the adsorbate [46]. The negative ΔG° demonstrate that the process is thermodynamically feasible and the spontaneous nature of the adsorption [54]. Table 2 indicate that the values of ΔG° for Ni at lower temperatures are slightly positive, and ΔG° decreases to lower values with rising temperature. It express that the adsorption process is less favored at lower temperature. The positive and small values of ΔG° were signified that the process was simple but non-spontaneous. Overall, the removal efficiencies were increased with increasing temperature [55].

Table 3
Element distribution of metal adsorbed and desorbed PAA hydrogel.

	AA	Cu Adsorbed	Cu Desorbed	Cd Adsorbed	Cd Desorbed	Ni Adsorbed	Ni Desorbed	Fe Adsorbed	Fe Desorbed
C (%)	51.69	49.99	50.91	51.35	50.45	46.96	49.99	38.71	47.80
O (%)	48.31	45.23	47.57	47.44	49.55	49.35	48.15	40.94	48.06
Cu (%)	–	4.79	1.52	–	–	–	–	–	–
Cd (%)	–	–	–	1.21	0.00	–	–	–	–
Ni (%)	–	–	–	–	–	3.68	1.86	–	–
Fe (%)	–	–	–	–	–	–	–	20.35	4.14

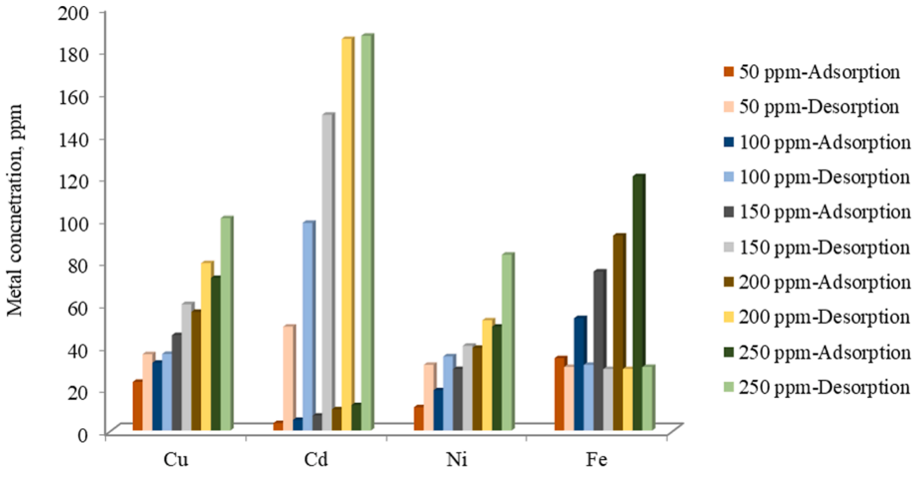

Fig. 8. The metal concentrations of supernatants after both adsorption and desorption.

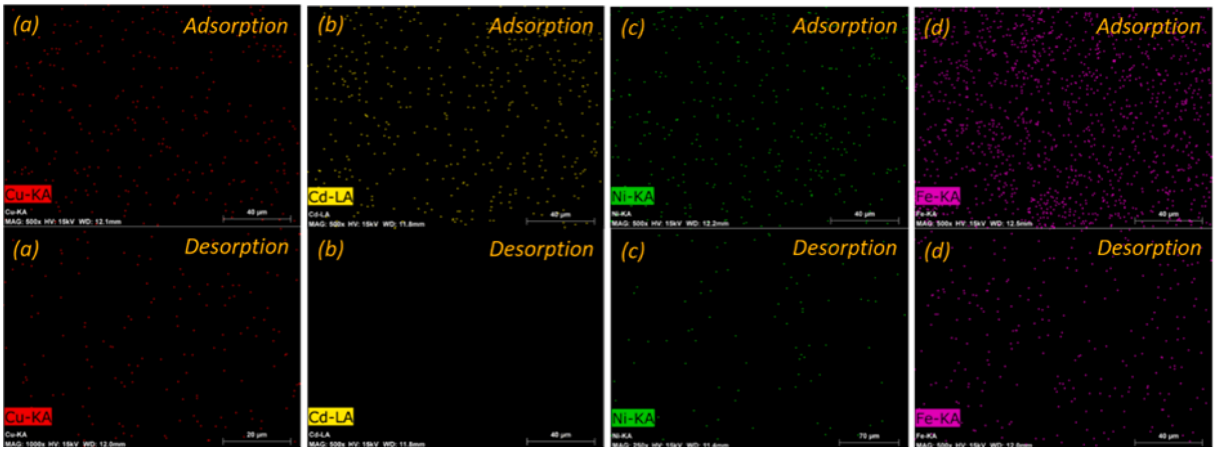

Fig. 9. Map images of the distribution of metal elements of hydrogels after 250 ppm metal adsorption (48 h) and release (48 h).

3.7. Desorption studies

One of the most important property of the adsorbent is its reusability. Reusability is superior property to reduce process cost. The reusability studies and importance of mechanism were reported in previous studies [56]. Desorption studies were done to specify the reusability of PAA-hydrogel. The metal concentrations of supernatants after both adsorption and desorption were given in Fig. 8. When the desorption results of each metal were examined, it was specified that as the adsorbed metal concentration increased, the amount of desorption increased and the desorption capacity of metals was Cd > Cu > Ni > Fe. The maximum desorption capacity was obtained in cadmium metal. When desorption studies of cadmium are examined, it is seen that desorption increases when concentration increases. However, no significant change was observed in the metal concentration of 200 ppm and 250 ppm.

Metal distribution in adsorption and desorption has also been demonstrated using by elemental mapping (Fig. 9). The apparently homogeneous colour change on the surface of the adsorbent explains that the PAA hydrogel adsorbs the metal ions homogeneously. The surface of the adsorbent is completely covered with metal ions. The amount of metal attached to the hydrogel surface decreased after release. This is proof of the re-usability of the hydrogel when the proper pH environment is provided. According to Fig. 9, the most metal-emitting was seen at PAA-Cd hydrogel. The fact that the Fe atom has the most element distribution in adsorption is because the folds on the surface are mostly seen in PAA-Fe depending on the pH.

The results of EDX analysis of metal adsorbed and after desorption of hydrogel at the same magnification are given in Table 3. Accordingly, the amount of metal accumulation taken from the surface of the gels after 48 h of 250 ppm adsorption and the mass percentages of the remaining metals after 48 h at pH 2 of the adsorbed hydrogels at

250 ppm for 48 h were compared. According to these results, the highest metal removal was observed in Cd^{2+} and the least was seen in Ni^{2+}. EDX analysis results are compatible with adsorption capacities.

4. Conclusion

In this study, eco-friendly PAA-hydrogels were produced and Cu^{+2}, Cd^{+2}, Ni^{+2} and Fe^{+3} heavy metals adsorption capacity have been examined. According to the adsorption experiments carried out under the same process conditions, the adsorption capacities of heavy metals were specified as Cd > Ni > Cu > Fe. It has been observed that the pH effect of the aqueous medium is quite high on the physical swelling behaviour of hydrogel. While the swelling values obtained by preserving the gel structure without being deformed with increasing pH, while benefiting from these features in adsorption and adsorbing a large amount of water, it also kept more metal ions in its body. In this way, while the capacity to hold metal ions at high pHs values, it was possible for gels at lower pH to release metal ions due to their shrinking behavior. This has enabled hydrogel to be re-used. Thus, PAA-based hydrogel, which is environmentally sensitive and used for wastewater treatment, have taken on the role of cleaning materials.

Funding

This manuscript was supported by Bilecik Seyh Edebali University Scientific Research Project (project number is 2018–01.BŞEÜ.11-02).

Availability of data and material: Not applicable.

Code availability (software application or custom code): Not applicable.

CRediT authorship contribution statement

F.O. Gokmen: Conceptualization, Methodology, Writing - original draft. **E. Yaman:** Validation, Investigation, Writing - review & editing. **S. Temel:** Formal analysis, Resources, Project administration.

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.

Acknowledgements

Bilecik Seyh Edebali University Scientific Research Project Commission supported this work financially (project number is 2018-01. BŞEÜ.11-02).The authors also thank to the Central Research Laboratory, Bilecik Seyh Edebali University for the characterization measurements.

References

[1] L.A. Shah, M. Khan, R. Javed, M. Sayed, M.S. Khan, A. Khan, M. Ullah, J. Clean. Prod. (2018), https://doi.org/10.1016/j.jclepro.2018.08.035.

[2] C. Chang, B. Duan, J. Cai, L. Zhang, Eur. Polym. J. (2010), https://doi.org/10.1016/j.eurpolymj.2009.04.033.

[3] D. Khodadadi-Dehkordi, Water Environ. J. (2018), https://doi.org/10.1111/wej.12309.

[4] S. Argin, P. Kofinas, Y.M. Lo, Food Hydrocolloids (2014), https://doi.org/10.1016/j.foodhyd.2014.02.018.

[5] N. Shirsath, D. Raghuvanshi, C. Patil, V. Gite, J. Meshram, Iran. Polym. J. (2018), https://doi.org/10.1007/s13726-018-0602-0.

[6] M.M. Ibrahim, M. Abd-Eladl, N.H. Abou-Baker, J. Appl. Polym. Sci. (2015), https://doi.org/10.1002/app.42652.

[7] N.K. Singh, D.S. Lee, J. Contr. Release (2014), https://doi.org/10.1016/j.jconrel.2014.04.056.

[8] J. Ma, X. Li, Y. Bao, RSC Adv. (2015), https://doi.org/10.1039/C5RA08522E.

[9] S. Sayyar, E. Murray, B. Thompson, J. Chung, D.L. Officer, S. Gambhir, G. M. Spinks, G.G. Wallace, J. Mater. Chem. B (2015), https://doi.org/10.1039/C4TB01636J.

[10] H. Li, A.M. Koenig, P. Sloan, N.D. Leipzig, Biomaterials (2014), https://doi.org/10.1016/j.biomaterials.2014.07.038.

[11] N. Gawande, A.A. Mungray, Separ. Purif Technol. (2015), https://doi.org/10.1016/j.seppur.2015.04.024.

[12] S. Thakur, B. Sharma, A. Verma, J. Chaudhary, S. Tamulevicius, V.K. Thakur, J. Clean. Prod. (2018), https://doi.org/10.1016/j.jclepro.2018.06.259.

[13] M. Khan, I.M. Lo, Water Res. (2016), https://doi.org/10.1016/j.watres.2016.10.008.

[14] Y. Li, G. Huang, X. Zhang, B. Li, Y. Chen, T. Lu, T.J. Lu, F. Xu, Adv. Funct. Mater. (2013), https://doi.org/10.1002/adfm.201201708.

[15] G.R. Mahdavinia, S. Mousanezhad, H. Hosseinzadeh, F. Darvishi, M. Sabzi, Carbohydr. Polym. (2016), https://doi.org/10.1016/j.carbpol.2016.04.024.

[16] W.W. Ngah, S. Fatinathan, Chem. Eng. J. (2008), https://doi.org/10.1016/j.cej.2007.12.006.

[17] E.M. Ahmed, J. Adv. Res. (2015), https://doi.org/10.1016/j.jare.2013.07.006.

[18] J.E. Efome, D. Rana, T. Matsuura, C.Q. Lan, J. Mater. Chem. A (2018), https://doi.org/10.1039/c7ta10428f.

[19] N.S. Alharbi, B. Hu, T. Hayat, S.O. Rabah, A. Alsaedi, L. Zhuang, X. Wang, Front. Chem. Sci. Eng. (2020), https://doi.org/10.1007/s11705-020-1923-z.

[20] X. Liu, H. Pang, X. Liu, Q. Li, N. Zhang, L. Mao, M. Qiu, B. Hu, H. Yang, X. Wang, Innovation (2021), https://doi.org/10.1016/j.xinn.2021.100076.

[21] J. Yu, Q. Lu, J. Zheng, Y. Li, Iran. Polym. J. (2019), https://doi.org/10.1007/s13726-019-00751-1.

[22] T. Gao, W. Wang, A. Wang, Macromol. Res. (2011), https://doi.org/10.1007/s13233-011-0706-2.

[23] M. Khan, L.A. Shah, T. Rehman, A. Khan, A. Iqbal, M. Ullah, S. Alam, Iran. Polym. J. (2020), https://doi.org/10.1007/s13726-020-00801-z.

[24] X. Yi, F. Sun, Z. Han, F. Han, J. He, M. Ou, J. Gu, X. Xu, Ecotoxicol. Environ. Saf. (2018), https://doi.org/10.1016/j.ecoenv.2018.04.039.

[25] M.R. Awual, M.M. Hasan, T. Ihara, T. Yaita, Microporous Mesoporous Mater. (2014), https://doi.org/10.1016/j.micromeso.2014.07.005.

[26] J.E. Efome, D. Rana, T. Matsuura, C.Q. Lan, Chemical Engineering Journal (2018), https://doi.org/10.1016/j.cej.2018.07.077.

[27] J.E. Efome, D. Rana, T. Matsuura, C.Q. Lan, Sci. Total Environ. (2019), https://doi.org/10.1016/j.scitotenv.2019.04.187.

[28] I. Anastopoulos, A. Bhatnagar, E.C. Lima, J. Mol. Liq. (2016), https://doi.org/10.1016/j.molliq.2016.06.076.

[29] J.E. Efome, D. Rana, T. Matsuura, C.Q. Lan, A.C.S. Appl, Mater. Interfaces (2018), https://doi.org/10.1021/acsami.8b01454.

[30] N. Johri, G. Jacquillet, R. Unwin, Biometals (2010), https://doi.org/10.1007/s10534-010-9328-y.

[31] D. Schaumlöffel, J. Trace Elem. Med. Biol. (2012), https://doi.org/10.1016/j.jtemb.2012.01.002.

[32] B.R. Stern, J. Toxicol. Environ. Health A (2010), https://doi.org/10.1080/15287390903337100.

[33] X. Ding, L. Song, Y. Han, Y. Wang, X. Tang, G. Cui, Z. Xu, Biomed Res. Int. (2019), https://doi.org/10.1155/2019/8591631.

[34] J. Duruibe, M. Ogwuegbu, J. Egwurugwu, Int. J. Phys. Sci. 5 (2007) 112.

[35] B. Lam, S. Deon, N. Morin-Crini, G. Crini, P. Fievet, J. Clean. Prod. (2018), https://doi.org/10.1016/j.jclepro.2017.10.090.

[36] A.A. Alqadami, M.A. Khan, M. Otero, M.R. Siddiqui, J. Byong-Hun, K.M. Batoo, J. Clean. Prod. (2018), https://doi.org/10.1016/j.jclepro.2018.01.023.

[37] H. Du, Z. Ren, Y. Xu, Iran. Polym. J. (2018), https://doi.org/10.1007/s13726-018-0638-1.

[38] X. Han, W. Wang, X. Ma, Chem. Eng. J. (2011), https://doi.org/10.1016/j.cej.2011.02.067.

[39] W. Kong, Q. Yue, Q. Li, B. Gao, Sci. Total Environ. (2019), https://doi.org/10.1016/j.scitotenv.2019.03.095.

[40] X. Gao, W. Li, H. Ma, J. Alloy. Compd. (2019), https://doi.org/10.1016/j.jallcom.2019.07.057.

[41] S. Temel, F.Ö. Gökmen, E. Yaman, Acad. Platform J. Eng. Sci. (2020), https://doi.org/10.21541/apjes.529000.

[42] P.B. Vilela, C.A. Matias, A. Dalalibera, V.A. Becegato, A.T. Paulino, J. Environ. Chem. Eng. (2019), https://doi.org/10.1016/j.jece.2019.103327.

[43] Y. Zheng, S. Hua, A. Wang, Desalination (2010), https://doi.org/10.1016/j.desal.2010.06.054.

[44] A. El-Halah, F. López-Carrasquero, J. Contreras, Ciencia e Ingeniería (2018) http://www.redalyc.org/articulo.oa?id=507555109006.

[45] Z. Lin, Y. Hu, Y. Yuan, B. Hu, B. Wang, Ecotoxicol. Environ. Saf. (2021), https://doi.org/10.1016/j.ecoenv.2020.111451.

[46] B. Dash, B. Dash, S.S. Rath, Sep. Purif. Technol. (2020), https://doi.org/10.1016/j.seppur.2020.116649.

[47] S. Nethaji, A. Sivasamy, Chemosphere (2011), https://doi.org/10.1016/j.chemosphere.2010.11.080.

[48] R.P. Han, P. Han, Z.H. Cai, Z.H. Zhao, M.S. Tang, J. Environ. Sci. (2008), https://doi.org/10.1016/S1001-0742(08)62146-4.

[49] F. Deniz, Mater. Sci. Eng. C (2013), https://doi.org/10.1016/j.msec.2013.03.009.

[50] D. Sun, X.D. Zhang, Y.D. Wu, X. Liu, J. Hazard. Mater. (2010), https://doi.org/10.1016/j.jhazmat.2010.05.015.

[51] M. El-Haddad, R. Slimani, R. Mamouni, M.R. Laamari, S. Rafqah, S. Lazar, J. Taiwan Ins. Chem. Eng. (2013), https://doi.org/10.1016/j.jtice.2012.10.003.

[52] C. Bai, L. Wang, Z. Zhu, Int. J. Biol. Macromol. (2020), https://doi.org/10.1016/j.ijbiomac.2019.09.249.

[53] F. Krika, N. Azzouz, M.C. Ncibi, Arab. J. Chem. (2016), https://doi.org/10.1016/j.arabjc.2011.12.013.

[54] F. Moghimi, A.H. Jafari, H. Yoozbashizadeh, M. Askari, Trans. Nonferrous Met. Soc. China (2020), https://doi.org/10.1016/S1003-6326(19)65195-2.

[55] Z.Y. Yao, J.H. Qi, L.H. Wang, J. Hazard. Mater. (2010), https://doi.org/10.1016/j.jhazmat.2009.09.027.

[56] Y. Zhu, X. He, J. Xu, Z. Fu, S. Wu, J. Ni, B. Hu, Chemosphere (2021), https://doi.org/10.1016/j.chemosphere.2020.127901.