O 40. PHOSPHATE REMOVAL FROM WASTEWATER BY USING CATIONIC COMPOSITE HYDROGELS

Demet Aydınoğlu[1*]

[1] *Yalova University, Armutlu Vocational School, Department of Food Process*

E-mail: daydinoglu@yahoo.com

ABSTRACT: Wastewater treatment and making it reusable is of great importance especially considering global warming and limited water sources on earth. One of the water pollutants is phosphate pollution caused by domestic wastes such as detergents and this pollution increases alg blooms, which leads to decrement in water quality. In this study, which is thought that anionic phosphate pollution can be easily removed with the help of cationic materials, the composite hydrogels consisiting of positive charged polymeric 3- acrylamido- trimethly ammonium chloride and chitosan were prepared. After various characterization tests, phosphate uptake capacities of the composite materials were determined. With the phosphate holding capacities attaining up to 124 mg / g and its reusabiliy up to 5 cycles, it was observed that the composite hydrogels have a potential to use for phosphate removal as an adsorbent.

***Keywords**: Hydrogel, Composite, Phosphate, Water Treatment.*

1. INTRODUCTION

Wastewater treatment and making it reusable has a great importance when it is considered to global warming and limited water resources on the earth. Currently, a number of different methods are applied in water treatment, from chemical precipitation to ion exchange, from electrochemical treatment to membrane technology and adsorption (Bisht et al. 2017). Among them, adsorption has attracted a great attention in terms of easy application and low cost (Volesky, 1997). It is well known from the literature that a high number of substances have the ability to serve as an adsorbent by removing the various pollutants such as heavy metals, textile dyes and the others etc. from wastewater.

Adsorbents can be classified into the two main groups: natural and synthetic adsorbents. Zeolit, clay and perlit, which are inorganic origin and also chitosan, cellulose, resin and hard fruit shell which are organic origin can be given as an example for natural adsorbents. Synthetic adsorbents, on the other hand, can be expensive in some cases, and because of their synthetic origin, their potential to harm the environment can be mentioned. However, they have the advantage that they can be designed with the desired feature. Many polymeric substances can be given as an example for the synthetic adsorbents (Demir and Yalçın, 2014).

Considering these points, especially in recent years, the synthesis of organic / inorganic hybrid hydrogels and its use in removal of impurities from wastewater is a remarkable subject. It is well known that the use of such materials in wastewater treatment has given promising results. For example, in many studies carried out with these hybrid hydrogels consisting of the combination of natural adsorbents such as montmorillonite clay, chitosan and cellulose with the synthetic adsorbents such as polyvinylalchol, polyacrylic acid and polymethylmethacrylate etc. and they have shown their applicability for water recycling process, producing high adsorption capacities reaching sometimes 99% for several cationic pollutants (Moreno-Sader et al.,2019; Mohsenl et al., 2017; Bunhu et al., 2016; Maskawat Marjub et al., 2019; Abdeen et al., 2015; Godiya et al., 2018)

Similar to the cationic ones, also various anionic pollutants can be removed from wastewater by using adsorbents, as well. For this generally the substances with cationic property are benefited. In the literature, there are different studies, investigate the adsorption of several anionic pollutants such as anionic dyes, nitrate, nitrite, cyanide, perchlorate, and fluoride ions etc. (Yang et al., 2020; Anees and Jishna, 2017; Moghadam et al., 2018; Ilgin et al., 2020; Zheng et al., 2014; Xie et al., 2010; Arcos-Arévalo et al., 2016). In these studies, polystyrene functionalized with triethylamine groups and quaternized chitosan has being drawn attention as an adsorbent.

In addition to the abovementioned anionic ones, phosphate is also the one of the anionic pollutants and is caused by domestic wastes such as detergents, leading to decrement in water quality by increasing algae blooms. Generally the adsorbents having cationic groups on their surface are used for effective phosphate anions. In the literature there are some examples for this. In particular the ones with amine functionalized and quaternary amine groups have received great interest about this issue (Shen et al., 2015; Wu et al., 2017; Yousif et al., 2015)

In this study it was aimed at preparation of an effective cationic adsorbent for removal of phosphate anions from water. In order to enhance the adsorption capacity of the adsorbent, it was attempted to incorparation of chitosan into poly(Acrylamide-co-3-methacrylamido-N,N,N-trimethylpropan-1-aminium chloride) (p(AAm-co-MAPTAC) network and in this way it was synthesized semi-IPN hydrogels composed of poly(Acrylamide-co-3-methacrylamido-N,N,N-trimethylpropan-1-aminium chloride) (p(AAm-co-MAPTAC) and chitosan. With these prepared cationic hydrogels, it was created a syntergetic effect.

The new hydrogels prepared with the abovementioned purpose were also exposed to several characterization test to better understand their adsorption behaviour.

2. MATERIAL AND METHOD

2.1. Materials

Acrylamide (AAm), 3-methacrylo propyl trimethyl ammonium chloride (MAPTAC) and N,N-methylene bisacrylamide (BAAm), which were used as main monomer, comonomer and crosslinker, respectively and also chitosan, which was used as linear polymer were all bought from Aldrich Chemicals (Milwaukee, WI,USA). Ammonium peroxydisulfate (APS) and sodium meta bisulfite (SMBS), which were employed as redox initiator pair, were purchased from Merck (Darmstad, Germany). Acetic acid and sodium hydroxide, used for preparation of the hydrogels and also sodium dihydrogen phosphate for adsorption experiments, were supplied by Aldrich Chemicals (Milwaukee, USA). Ammonium molybdate tetra hydrate, tin chloride dihydrate and glycerine, which were used for determination of the amount of phosphate ions, were all purchased from Aldrich Chemicals (Milwaukee, WI, USA).

2.2. Preparation of hydrogels

Poly(AAm-co-MAPTAC)-chitosan semi-IPN hydrogels were prepared by using free radical polymerization in presence of chitosan, utilizing BAAm as crosslinking agent. The synthesis schema was depicted in Figure 1. Briefly, predetermined weights of AAm and BAAm were dissolved in aqueous acetic acid solution (1% wt.) under magnetic stirring. MAPTAC, APS and SMBS were then inserted into the mixture in turn and obtained pre-gel solution were poured into the air-tight glass tubes in water bath at 35 °C for 24 hours. After 24 hours, the hydrogels were removed from the tubes and cut into as discs. To prevent chitosan molecules from dissolution in water, the gel discs were immediately immersed in 1 M NaOH solution and allowed to neutralization for for one hour. Afterwards, they were taken from the basic solution and transferred into deionized water for purification. The fully swollen hydrogels were dried in freeze-dryer and named as MX-CY, where X and Y represent the molar ratio of MAPTAC and the weight of chitosan, respectively. The hydrogel compositional ratios are tabulated in Table 1.

Table 1. The hydrogel compositional ratios.

Hydrogel	AAm ($x10^{-2}$ moL)	MAPTAC ($x10^{-2}$ moL)	BAA($x\ 10^{-4}$ moL)	Chitosan (g)
A-5M-0.1C	0.95	0.05	1.67	0.1
A-5M-0.2C	0.95	0.05	1.67	0.2
A-10M-0.1C	0.90	0.10	1.67	0.1
A-10M-0.2C	0.90	0.10	1.67	0.2

2.2. Swelling measurements of the hydrogels

To find the swelling capacities of hydrogels, the dry gel samples were placed in deionized water and weighed at certain intervals until they reached a constant weight, which means swelling equilibrium. The swelling degrees of the hydrogels were calculated by using the following equation:

$$Sw = \frac{m_s - m_d}{m_d} \tag{1}$$

where S_w, m_s and m_d show the equilibrium swelling percent, weights of swollen and dry hydrogels, respectively.

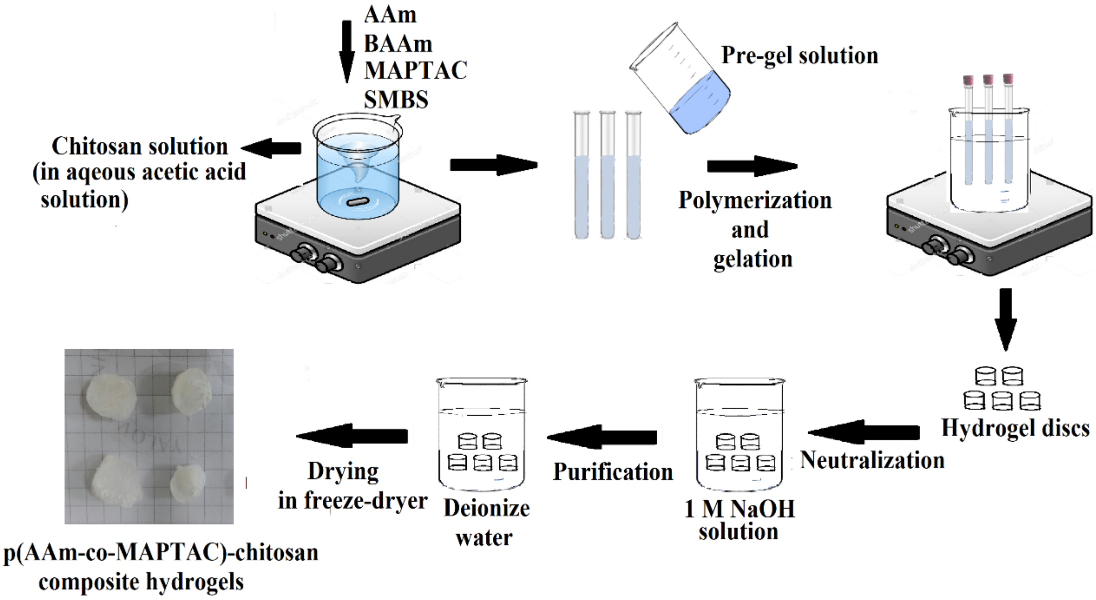

Figure 1. Synthesis schema of the p(AAm-co-MAPTAC)/chitosan hydrogels.

2.3. Mechanical tests of the hydrogels

The gel strengths of the hydrogels were identified by employing compressing test. The swollen samples having approximately 1 cm of the length were subjected to uniaxial compression by using Zwick/Roell Z1.0 universal testing machine (Zwick Gmb&Co.KG,Ulm,Germany) equipped with a 50-N load cell at a compression rate of 3 mm/min. The compression was maintained up to 60% of the deformation ratio and the compression force values versus the deformation percentages were monitored.

2.4. Adsorption tets of the hydrogels

To study the adsorption capacity of the hydrogels, it was utilized from batch-adsorption technique. According to this technique, the dry hydrogel discs of which weights are about 0.1 g were immersed in 100 mL of 50 ppm of PO_4^{3-} solution, and both the initial concentrations and those at certain time intervals were determined by using the standard molybdenum blue spectrophotometric methodat 690 nm (APHA-method-4500-P) (American Public Health Association. 1999. Standard methods for the examination of water and wastewater. Washington DC). The phosphate adsorption capacity of the hydrogels were calculated as qe (mg/ g) by using the following equation (Eaton et al., 2005) :

$$q_e = \frac{\sum(c_i - c_f)x\ V}{W} \tag{2}$$

where, c_i and c_f show the phosphate concentrations in the solutions at initial and t time (mg/L), respectively. V and W denote the volume of the phosphate ion solution and the dry weight of the hydrogel, respectively. To find out the adsorption isotherm models of the hydrogels, the adsorption measurements were repeated with different PO_4^{3-} concentrations (50, 500, 300, and 450 ppm).

3. RESULTS AND DISCUSSIONS

3.1. Swelling behaviour of the hydrogels:

The swelling degrees of the hydrogels are seen in Figure.2 as a function of time. As seen in the figure, the all hydrogels continue to swell for approximately six hours and reached a plataeu which means to swelling equilibrium.

It was found that the maximum swelling degree was achieved with A-10M-0.2C hydrogel had a value of 251.21 g/g. The test results showed an increase of both the MAPTAC and chitosan ratios in the hydrogel composition resulted in increment in the water adsorption capacities. When these two parameter was analysed separately, it can be stated that the effect of chitosan on the swelling extents of the hydrogels was more obvious in the hydrogels containing 10% of MAPTAC. This can be attributed to high ionic content of the main matrix of the A-10M hydrogels. Most probably due to fact that the high ionic content of A-10M hydrogels enables the hydrogel more extended, which leads to better distribution of chitosan chains in this matrix. It seems that at this combinational ratio, chitosan chains were homogenously distributed and their functional groups, especially amine groups, were open form which are ready to capture more water molecules. The maximum swelling degrees of the hydrogels are given in Table.2

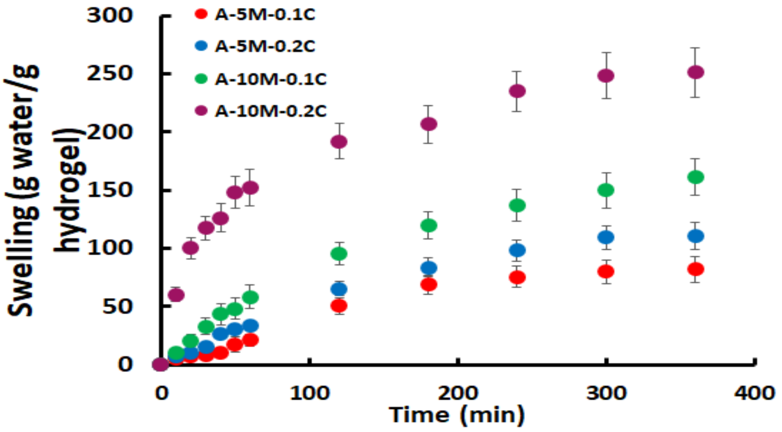

Figure 2. Swelling curves of the hydrogels in deionized water at 25 ºC.

3.2. Mechanical behaviour of the hydrogels:

The gel strengths of the hydrogels were presented in Table 2 together with the maximum swelling degrees. As seen in the table that the hydrogels were observed to withstand to the compression force up to 1.11 N as maximum.

Table 2. Maximum swelling degrees and compressional strengths of the hydrogels

Hydrogel	Maximum Swelling Degree (g/g)	Maximum Compression Strength (N)
A-5M-0.1C	82.15	0.72
A-5M-0.2C	111.08	1.11
A-10M-0.1C	131.41	0.62
A-10M-0.2C	251.21	0.40

The test results indicated that the lowest gel strength was exhibited by A-10M-0.2C most probably due to its high swelling degree, which generally cause the hydrogel to have poor mechanical property. According to the results it can be infer that both MAPTAC and chitosan contents create lower maximum compression strength. However, interestingly, an increase of chitosan in the hydrogels having 5% of MAPTAC resulted in reduction in gel strengths. This fact can be attributed to increased polymer density with the rise in chitosan content. In fact the same trend was not observed for the hydrogels having 10% of MAPTAC. This different result might be linked to great adsorption capacity of A-10M hydrogels, which possibly generates highly expanded network and thus, lower the polymer density. Therefore, most probably increase of chitosan content did not cause to rise in polymer density and thus leads not to lower gel strengts.

3.3. Adsorption behaviour of the hydrogels:

The hydrogels were found to have high phosphate adsorption capacities (q_e) as expected from the high number of cationic groups they have (Figure.3). It is seen from the figure that the hydrogel adsorb more amount of phosphate ions as the initial concentration of the outer solution increases.

To find out the adsorption behaviour of the hydrogels and to determine their maximum adsorption capacities (q_m) the mostly used two adsorption models (Freundlich and Langmuir isotherm models) were employed. They are expressed as the following equations, respectively:

$$LN(q_e) = LN(K_F) + \left(\frac{1}{n}\right) LN(c_e) \tag{3}$$

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_m}\right)\left(\frac{1}{c_e}\right) + \left(\frac{1}{q_m}\right) \tag{4}$$

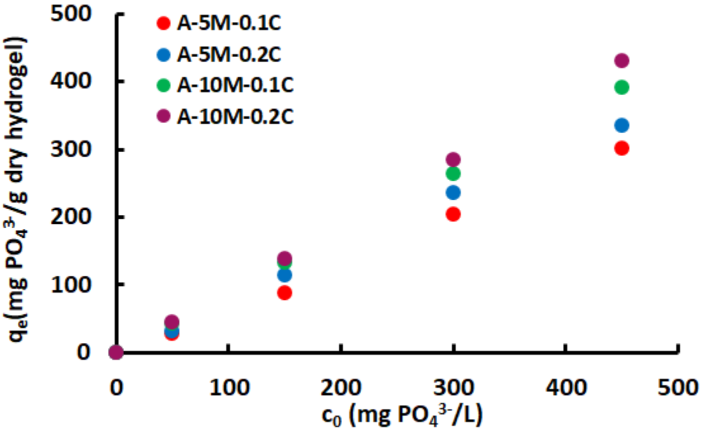

Figure 3. Adsorption capacities of the hydrogels (q_e) depending on the different initial concentration of phosphate ions (c_0) .

According to the Freundich adsorption model, described as Equation.3, the plots of LN(qe) versus LN(ce) yield straight lines, of which slope and intercept values are equal to the inverse of the adsorption intensity (1/n) and logarithmic form of the Freundlich adsorption capacity (LN(K_F)), respectively. The isotherms prepared by appliying the experimental results to this model were shown in Figure 4. Also the calculated Freundlich constants and the related parameters are seen in Table 3.

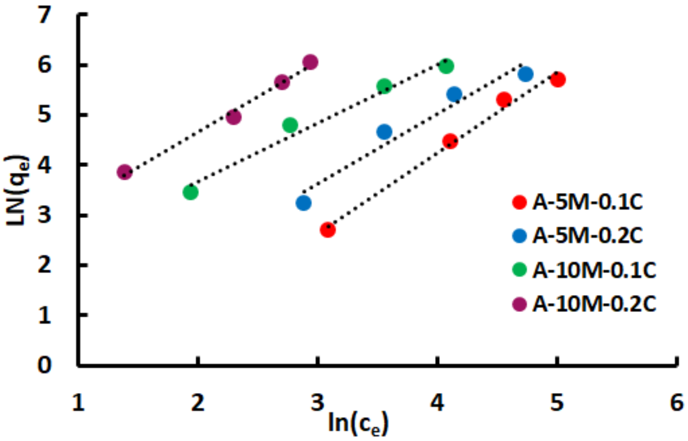

Figure 4. Freundlich isotherms of the hydrogels.

On the other hand also Langmuir isotherms model was examined for the adsorption behaviour of the hydrogels. For this the related expression which is seen in Equation.4 was employed. Basis on this model, it is seen that the plots between $1/q_e$ and $1/c_e$ produce straight lines of which slope and intercept values give the Langmuir isotherm constants (K_L) and the maximum adsorption capacity (q_m), respectively. In order to the applicability of the adsorption behaviour of the hydrogels for this model, the plots between $1/q_e$ and $1/c_e$ were prepared and used for calculation of Langmuir isotherm constants (K_L) and the maximum adsorption capacity (q_m).(Figure 5). Also the calculated Langmuir constants and the related parameters are seen in Table 3.

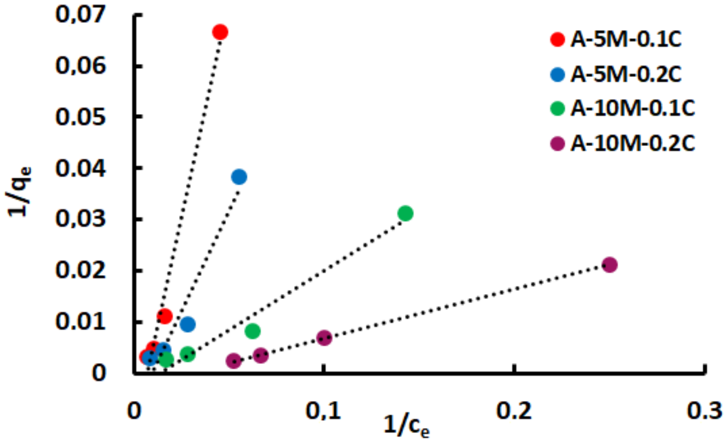

Figure 5. Langmuir isotherms of the hydrogels.

Table. 3. Freundlich and Langmuir constants of the hydrogels.

Hydrogel Type	FREUNDLICH MODEL			LANGMUIR MODEL		
	n	K_F	R^2	q_m	$K_L \times 10^{-3}$	R^2
A-5M-0.1C	0.619	0.109	0,9887	81.97	7.14	0.9857
A-5M-0.2C	0.720	0.587	0,9463	133.33	9.56	0.9424
A-10M-0.1C	0.856	3.821	0,9747	322.58	13.32	0.9734
A-10M-0.2C	0.711	6.367	0,9921	357.14	29.07	0.9999

The correlation coefficients (R^2) of the Freundlich and Langmuir models are seen to close to one, which indicates that the both models fit to the experimental results, well. It is known that this result mostly occurs when the adsorption capacity of an adsorbent is too high kile in the case of this study. Most probably, for this reason the both model was well correlated with the experimental results. On the other hand, it was found that Freundlih adsorption capacity (K_F) was ranged between 0.109 and 6.367, increasing with increment in the ionic content of the hydrogel. This means that the more cationic content a gel has, the more phosphate ions are adsorbed. As to Langmuir model, the model gave the maximum adsorption capacities of the hydrogels, which rise with positively charged groups, as expected. It was understood that A-10M-0.2C hydrogel had a maximum adsorption capacity of 357.14 mg/g.

4. CONCLUSIONS

In this study a composite hydrogel carrying of strong cationic groups were successfully synthesized for phosphate adsorption. The hydrogels were found to have great swelling degrees ranged between 82.15 and 251.21 g/g, increasing with increment in both MAPTAC and chitosan amounts. The mechanical test results, on the other hand showed that the hydrogels withstand to 1.11N as maximum, depending on its compositional ratios. The present p(AAm-co-MAPTAC)-chitosan composite hydrogels have exhibited great phosphate adsorption capacity reaching up to 357.14 mg phosphate ion per gram of dry hydrogel. This result suggests that the poly(AAm-co-MAPTAC)-chitosan hydrogels are promising canditates for use an adsorbent for removal of phosphate anions from wastewater.

Acknowledge: *This study has been financially supported by Yalova University Scientific Research Projects Coordination Department (Project no. 2018.AP.0010).*

REFERENCES

Abdeen, Z., Mohammad, S. G., Mahmoud, M. S. , 2015, Adsorption of Mn (II) ion on polyvinyl alcohol/chitosan dry blending from aqueous solution. *Environmental Nanotechnology, Monitoring & Management*, 3, 1–9.

Aneesh, P., Jishna, M., 2017, Adsorption of Nitrates Using Quaternized Chitosan Resin. *J Chem Eng Process Technol.* 8 (5), 1-7.

Arcos-Arévalo, A. J., Zavala-Arce, R. E., Ávila-Pérez, P., García-Gaitán, B., García-Rivas, J. L., Jiménez-Núñez, M. de la L., 2016, Removal of Fluoride from Aqueous Solutions Using Chitosan Cryogels. *Journal of Chemistry*, 2016, 1–13.

Bisht, R., Agarwal, M., Singh,K., 2017, Methodologies for removal of heavy metal ions from wastewater: an overview. *Interdisciplinary Environmental Review*, 18(2), 124-142.

Bunhu, T., Tichagwa, L., & Chaukura, N., 2016, Competitive sorption of Cd^{2+} and Pb^{2+} from a binary aqueous solution by poly (methyl methacrylate)-grafted montmorillonite clay nanocomposite. *Applied Water Science,* 7(5), 2287–2295.

Demir, E., Yalçın, H., 2014, Adsorbentler: Sınıflandırma, Özellikler, Kullanım ve Öngörüler, *Türk Bilimsel Derlemeler Dergisi* 7 (2): 70-79.

Eaton, ADCLS, Greenberg, A.E, Franson, M.A.H., 2005, In: Eaton AD (ed) Standard methods for the examination of water and wastewater. American public health association, Washington DC, p 49

Godiya, C. B., Cheng, X., Li, D., Chen, Z., Lu, X., 2018, Carboxymethyl cellulose/polyacrylamide composite hydrogel for cascaded treatment/reuse of heavy metal ions in wastewater. *Journal of Hazardous Materials*., 364, 28-38.

Ilgin, P., Ozay, H., Ozay, O., 2020, The efficient removal of anionic and cationic dyes from aqueous media using hydroxyethyl starch-based hydrogels. *Cellulose*, 27, 4787–4802.

Maskawat Marjub, M., Rahman, N., Dafader, N. C., Sultana Tuhen, F., Sultana, S., Tasneem Ahmed, F., 2019, Acrylic acid-chitosan blend hydrogel: a novel polymer *adsorbent for adsorption of lead(II) and copper(II) ions from wastewater. Journal* of Polymer Engineering, *Journal of Polymer Engineering*, 39 (10) , 883-891.

Moghadam, F., Bagheri, S., Khamar. M., 2018, Evaluation of Chitosan Adsorbent Efficiency in Nitrate Removal from Aqueous Solutions and the Effect of Parameters on Adsorption Process. *International Journal of Innovative Science, Engineering & Technology*, 5 (5), 83-86.

Mohsen, M., Gomaa, E., Nabila Ahmed Mazaid N.A., Mohammed, R., 2017, Synthesis and characterization of organic montmorillonite-polyvinyl alcohol-co-polyacrylic nanocomposite hydrogel for heavy metal uptake in water, *AIMS Materials Science*,, 4(5): 1122-1139.

Moreno-Sader, K., García-Padilla, A., Realpe, A., Acevedo-Morantes, M., Soares, J. B. P. ,2019, Removal of Heavy Metal Water Pollutants (Co^{2+} and Ni^{+2}) Using Polyacrylamide/Sodium Montmorillonite (PAM/Na-MMT) Nanocomposites. *ACS Omega*, 4(6), 10834–10844.

Shen, H., Wang, Z., Zhou, A., Chen, J., Hu, M., Dong, X., Xia, Q., 2015, Adsorption of phosphate onto amine functionalized nano-sized magnetic polymer adsorbents: mechanism and magnetic effects. *RSC Advances,* 5(28), 22080–22090.

Xie, Y., Li, S., Wang, F., Liu, G., 2010, Removal of perchlorate from aqueous solution using protonated cross-linked chitosan. *Chemical Engineering Journal*, 156(1), 56–63.

Wu, Z., Gao, D., Liu, N., 2017, Adsorption behavior of phosphate on anion-functionalized nanoporous polymer. *Water Quality Research Journal*, 52(3), 187–195.

Volesky, B., 1994, Advances in biosorption of metals: selection of biomass types. *FEMS Microbiol. Rev.*14 (4), 291–302.

Yang, W., Wang, J., Shi, X., Tang, H., Wang, X., Wang, S., Zhang, W., Lu, J., 2020, Preferential Nitrate Removal from Water Using a New Recyclable Polystyrene Adsorbent Functionalized with Triethylamine Groups. *Ind. Eng. Chem.* 59 (11), 5194–5201.

Yousif, A. M., Atia, A. A., Zaid, O. F., Ibrahim, I. A., 2015, Efficient and Fast Adsorption of Phosphates and Sulphates on Prepared Modified Cellulose. *Journal of Dispersion Science and Technology*, 36(11), 1628–1638.

Zheng, W., Wang, Y., Yang, L., Li, X., Zhou, L., Li, Y., 2014, Novel adsorbent of polymeric complex derived from chaleting resin with Cu(II) and its removal properties for cyanide in aqueous solution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 455, 136–146.