Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

Removal of **Phosphate Ions from Wastewater** by Treated Hydrogel Based on Chitosan

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CHITOSAN/ Gelatin/2-(Dimethylamino) ethyl methacrylate (Cs/Gltn/PDMAEMA) hydrogel was synthesized by gamma irradiation for the expulsion of phosphate ions from wastewater. Chemical adjustment of the hydrogel with thiourea was performed to introduce thiol groups Cs/Gltn/PDMAEMA-treated. Moreover trapping of SiO_2 into the hydrogel matrix to acquire Cs/Gltn/PDMAEMA/SiO_2 composite. It was found that the gelation increases with increasing PDMAEMA content in the hydrogel. The maximum gelation performed at an equal ratio of Cs/Gltn at a radiation dose of 15 kGy. The adsorption capacities of the prepared systems towards phosphate ions were investigated. It was obtained that the maximum removal is achieved at pH 6 through 180 min. However, the removal percent decreases with increasing phosphate ions concentration and temperature. The ability of the prepared adsorbents towards phosphate ions removal are ascending ordered in the sequence of Cs/Gltn/PDMAEMA hydrogel, Cs/Gltn/PDMAEMA-treated , and Cs/Gltn/PDMAEMA/SiO_2 composite. The pseudo second-order equation fits well the adsorption kinetics. The adsorption isotherm follows the Freundlich model higher than the Langmuir model

Keywords: Adsorption, Composite, Hydrogel, Phosphate removal, Water treatment, Chitosan, Gamma irradiation.

Introduction

Phosphorus is found as phosphate $(PO_4)^{3-}$ in nature, the three fundamental wellsprings of phosphorus are livestock waste, human waste and farming fertilizers [1]. Phosphate particles are notable to significantly affect biological communities and can harm the wellbeing of waterways and lakes [2]. The expanding phosphor focuses in surface waters raise the growth of phosphate-dependent organisms, such as algae and duckweed [3] These living beings utilize incredible measures of oxygen and keep daylight from entering the water [4]. Moreover, the excessive amount of phosphate can cause medical issues, for example, kidney harm [5] and other chronic diseases [6]. In light of these contemplations, phosphate expulsion from wastewaters has turned into a natural necessity [7]. Numerous techniques are utilized for the evacuation of phosphate, including the chemical, Physiochemical and biological methods [8]. The physicochemical strategies for phosphate particle evacuation utilizing polymer hydrogels are the best and reliable. Chitosan is a cationic biopolymer gotten by a full or fractional N-deacetylation of chitin, which is known as a noteworthy part of the shellfish exoskeletons [9]. It has been demonstrated to have attractive

characteristics, for example, hemostasis, bacteriostasis, and biocompatibility [10]. It has hydroxyl and amino functional groups that make chitosan available in different applications such as the expulsion of metal particles, anions, and dyes [11]. Moreover, some chemical substituents are made with respect to these functional groups to improve the adsorption properties such as thionyl groups [12].

This investigation plans to the preparation of a biodegradable, ease, and powerful adsorbent for expulsion of phosphate ions from watery arrangements. Attributable to the basic properties of amino groups as particular sorbents of acidic groups [13]. Cs/Gltn/PDMAEMA hydrogel was set up by gamma radiation. Chemical adjustment of the readied hydrogel with thiourea was done to introduce thiol groups, Cs/Gltn/PDMAEMA-treated. Moreover trapping of SiO_2 into the hydrogel matrix to acquire Cs/Gltn/PDMAEMA/ SiO_2 composite. Every single arranged framework was focused as adsorbents for removal of phosphate ions from wastewater. The controlling adsorption variables were streamlined.

Experimental

Materials

Chitosan (Cs) (85% DA) of medium molecular weight was supplied from Meron. Gelatin was supplied from El-Nasr Pharmaceutical Chemical-Prolabo (Cairo, Egypt). 2-(N,N-Dimethylamino) ethyl methacrylate (DMAEMA) and silicon dioxide (SiO_2) were supplied from (Sigma-Aldrich, USA). Other chemicals were purchased from El-Nasr Co. (Cairo, Egypt).

Synthesis of Cs/Gltn/PDMAEMA hydrogel

A 1.5% Cs solution (w/v) containing 1% (v/v) acetic acid was stirred for 1h at 60 °C in the water bath with. A solution (w/v) of 20% gelatin was set up by dissolving 20g of gelatin in 80 mL of deionized water at 60 °C for 30 min in the water bath. In this manner, the two solutions were poured together in different proportions. DMAEMA was added to the solution in different proportions. The mixture was irradiated at different irradiation doses using ^{60}Co gamma source. The readied hydrogel was separated in distilled water for 2h at 80 °C to evacuate the non-cross linked polymer at that point air-dried.

Synthesis of Cs/Gltn/ PDMAEMA/ SiO₂ composite

A 0.03 g of SiO_2 powder was added to a 98.5 mL of deionized H_2O containing 1% (v/v) acetic acid solution and sonicated for 30 min. At that

point, 1.5 g of the Cs was included and mixed at 60°C for 1 h in the water bath. Thus, the above strides for the planning of Cs/Gltn/PDMAEMA hydrogel were pursued.

Synthesis of the treated Cs/Gltn/PDMAEMA hydrogel

A 15 g of Cs/Gltn/PDMAEMA hydrogel, 15g Thiourea, 50 mL HCl and 150 mL H_2O were stirred for 24 h [14]. The swelled hydrogel was washed and exchanged to another flask containing 10% (w/v) NaOH and subjected to a magnetic stirring for another 6h. After filtration, the hydrogel washed with acetone, ethanol, and deionized water. Finally, it was dried at 50°C.

Adsorption Study

Determination of phosphate was carried out in a 25 volumetric flask, by taking 1 ml of sample with 2 ml of 2.5 % ammonium molybdate and 0.5 ml of 10 N sulfuric acid solutions. After shaking well 1 ml of 0.5 M hydrazine hydrate solution was added and complete the volume up to mark by distilled water. The maximum color was developed after 45 min. So, measure the absorbance at 840 nm. Calculate the amount of phosphate in ppm (mg/L) from calibration curve[15]

Results and Discussion

Preparation of Cs/Gltn/PDMAEMA hydrogel

Figure 1 demonstrates the impact of copolymer composition on gel fraction of (Cs/Gltn/ PDMAEMA) hydrogel at DMAEMA fixation 0.07252 (g/g) It tends to be seen that the gel fraction of the hydrogel changed in connection to the Cs/Gltn composition which achieved the maximum value at equal content of Cs / Gltn. This was attributed to the hydrogen bond development between (-COOH, -OH and $-NH_2$) groups in gelatin and (-OH and $-NH_2$) groups in chitosan resulting in a compact structure, which showed more gel fraction [16]. It is clearly observed that as the content of Cs is significantly higher than that of Gltn, an abatement in gelation was acquired. This is on account of the rate of development of the homopolymer was higher than the copolymer crosslinked arrangement. The impact of gamma radiation doses on the gel fraction of Cs/Gltn/ PDMAEMA hydrogels was researched and appeared in Fig. 2. The figure demonstrates that, the gel percent increments with the expansion in radiation measurement up to 15 kGy and after that a little reduction was seen with additionally increment in radiation dosage unite. A drop in gelation was acquired at radiation dose 35 kGy. When a solution

of (Cs/Gltn/PDMAEMA) is irradiated with g-rays, free radicals are produced from water, and monomers. Irregular responses of these radicals cause polymerization and development of a network. The gamma irradiation dose has two inverse impacts; crosslinking and degradation mpact. It is notable that, at high radiation dose the rate of radiation degradation might be quicker than that of radiation crosslinking therefore the gel portion diminishes at high irradiation dosages

[17, 18].

Figure 3 shows the effect of DMAEMA content on the gel fraction of Cs/Gltn/PDMAEMA hydrogel. It can be observed that the gel fraction of the hydrogel expanded with increasing the DMAEMA content. As the content of DMAEMA increase, more radicals are framed by the impact of gamma irradiation and hence a high crosslink
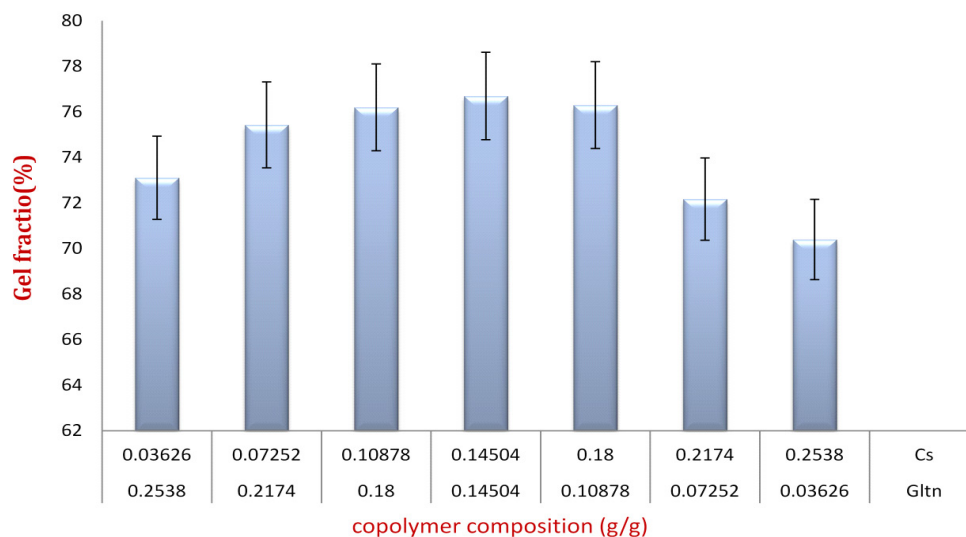

Fig. 1. Effect of copolymer composition on gel fraction of (Cs/Gltn/PDMAEMA) hydrogel, DMAEMA concentration; 0.0725(g/g) and total copolymer/monomer concentration; 0.36258 (g/g) at radiation dose;15 kGy.
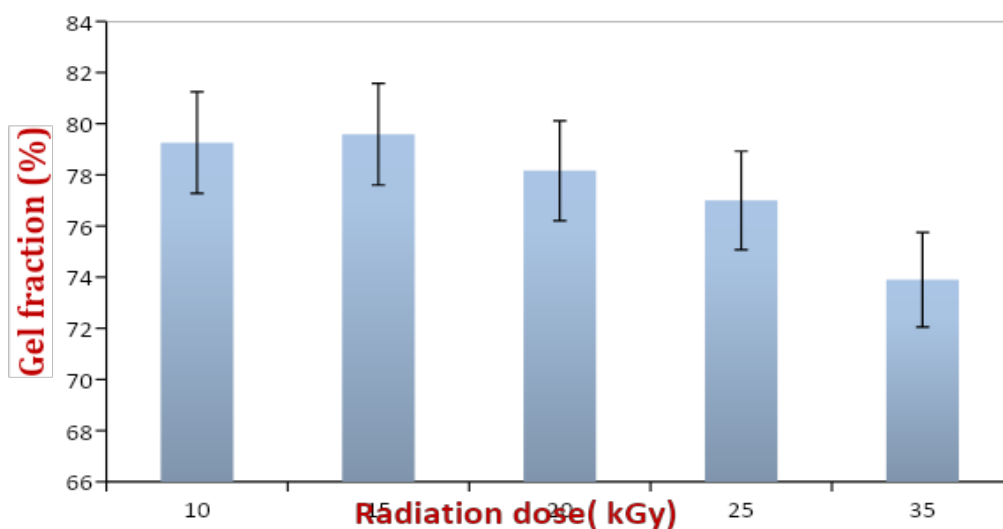

Fig. 2. Effect of radiation dose on gel fraction of (Cs/Gltn/PDMAEMA) hydrogel, at equal Cs/Gltn content and total copolymer/monomer concentration; 0.36258 (g/g).
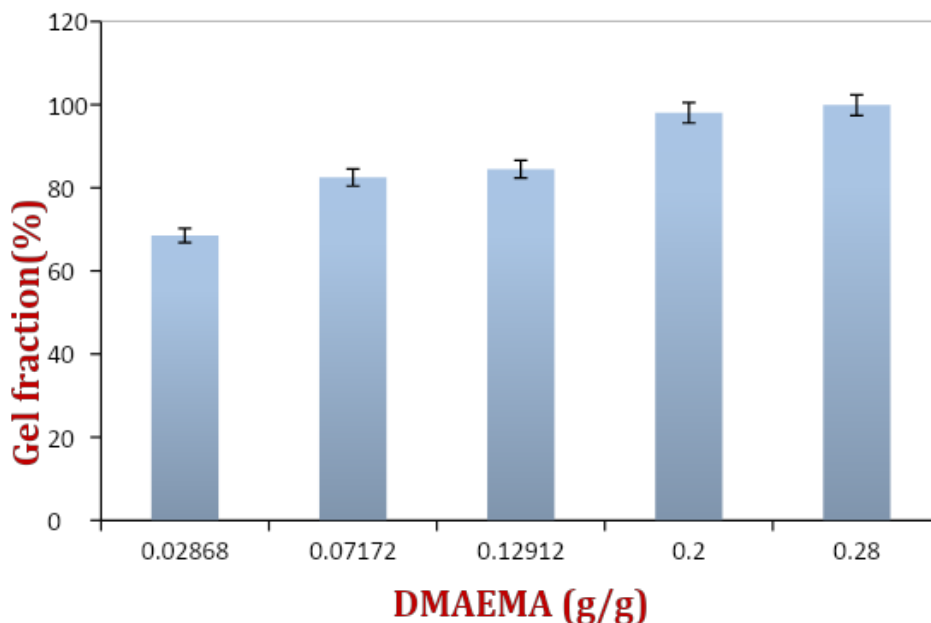
Fig. 3. Effect of DMAEMA concentration on gel fraction of (Cs/Gltn/PDMAEMA) hydrogel, at equal Cs/Gltn content and radiation dose; 15 kGy.

structure was acquired [16].

Treatment of Cs/Gltn/PDMAEMA hydrogel

The glucosamine repeating unit of chitosan has amine and two hydroxyl groups that can go about as a responsive site for chemical modification [19]. In most cases the modification is done by substituting these groups with carboxylic acid, or thionyl groups [20]. Treatment of chitosan may be justified by two purposes; preventing the dissolving of the polymer when metal sorption or desorption is performed in acidic solutions. Also, improving metal sorption capacities or selectivity [21]. Sulfur derivatives have been widely considered because of the high reactivity of sulfur capacities that increment the sorption capacity[22]. In this study, treatment of Cs/Gltn/PDMAEMA hydrogel with thiourea as explained in Scheme 1. These functional groups increase the density of sorption sites and this subsequent in an expansion in surface polarity and hydrophilicity of the polymeric network. Because of the hydrophilic conduct of polymer networks, they have a wonderful increment in swelling capacity when keeping in water, accordingly these systems are strikingly extended and expanded size of pores permit a quick diffusion of the pollutants.

Adsorption study

The effect of dosage of the adsorption of $H_2PO_4^-$ ions is shown in Fig. 4. It can be noted that the removal percent increased with the increase in the

adsorbent dose while the adsorption capacity was decreased. The increase of the removal percent due to increase the surface area of adsorbent whatever, increase the number of active sites which are available for adsorption leading to the increase in the removal percent [23]. However, the adsorption capacity decreased as the adsorbent dosage increased due to at a higher adsorbent dosage the available active sites on the adsorbent increased compared with the lower adsorbent dosage. So, these sites are not completely occupied with the adsorbate, $H_2PO_4^-$ ions, whatever the adsorbent capacity decreased [24].

Influence of time on the adsorption of $H_2PO_4^-$ by Cs/Gltn/PDMAEMA, Cs/Gltn/PDMAEMA-treated and Cs/Gltn/PDMAEMA/SiO$_2$ composite was researched as appeared in Fig. 5. It can be seen that the adsorption capacity towards $H_2PO_4^-$ ions expanded with expanding time for all frameworks until the point when it achieved balance at 180 min. It very well may be noticed that the adsorption rate was at first quick and abating the rate with time until balance. The underlying quick adsorption rate is most likely because of the high accessibility of active sites on the surface of the adsorbent. In addition, the attractive forces among $H_2PO_4^-$ and adsorbent surface fasting the dispersion into the network to achieve the equilibrium [25]. Cs/Gltn/PDMAEMA/SiO$_2$ composite revealed the highest estimations of adsorption pursued by Cs/Gltn/
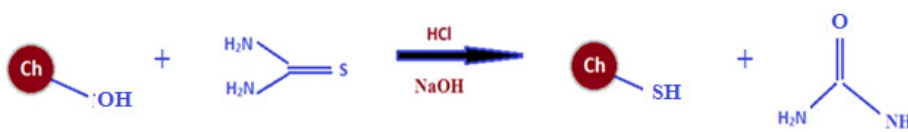
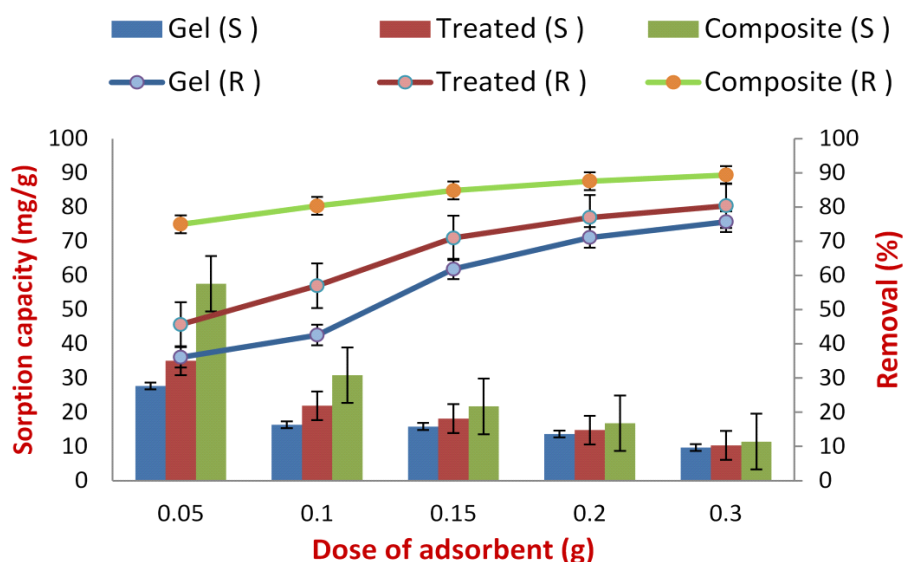**Scheme 1. The reaction of preparing the modified chitosan by thiourea.**

Fig. 4. The sorption capacity (S) and the removal percent (R) of $H_2PO_4^-$ as a function of the dose of adsorbent by Cs/Gltn/PDMAEMA, Cs/Gltn/PDMAEMA- treated and Cs/Gltn/PDMAEMA -SiO$_2$ composite, time; 240 min, initial concentration 192 mg/L, and pH;2
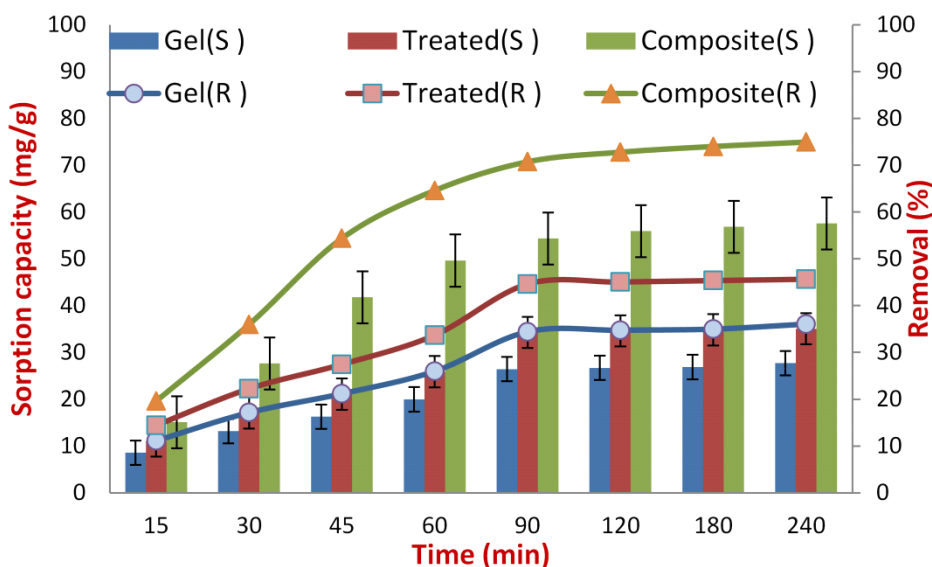

Fig. 5. The sorption capacity (S) and the removal percent (R) of $H_2PO_4^-$ as a function of time by Cs/Gltn/ PDMAEMA, Cs/Gltn/PDMAEMA- treated and Cs/Gltn/PDMAEMA -SiO$_2$ composite, pH;2, initial concentration 192 mg/L, and adsorbent dose; 2.5 g/L.

PDMAEMA-treated then Cs/Gltn/PDMAEMA hydrogel. The reason is that the higher number of active sites causes the adsorption capacity and removal percent to be expanded.

Figure 6 shows the removal percent and adsorption capacity of Cs/Gltn/PDMAEMA, Cs/Gltn/PDMAEMA-treated and Cs/Gltn/ PDMAEMA/SiO$_2$ composite as a function of the initial phosphate ions concentration. The removal percent decreased by increasing of H$_2$PO$_4^-$ ions concentration. This may be owing to the lack of available active sites required for the high initial concentration [26]. On the other hand, The sorption capacity for of H$_2$PO$_4^-$ ions increased with the increase in the initial concentration. It is well

known that the more concentrated the solution the better the adsorption due to increasing of the adsorbate ions, which increase the interaction probability with the adsorbent surface.

The effect of temperature on the removal of phosphate ions is shown in Fig. 7. It can be observed that the removal decreased with raising of temperature where the maximum sorption of phosphate ions was at 30 °C. This result indicated the exothermic nature of this adsorption processes onto the surface of all investigated systems. The rise in temperature may increase the tendency of desorption of ions from the interface to the solution[25].
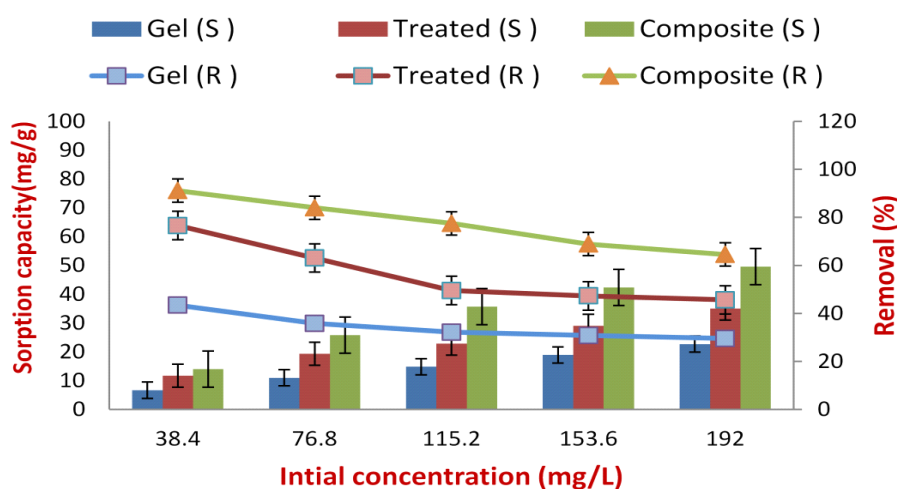

Fig. 6. The sorption capacity (S) and the removal percent (R) of H$_2$PO$_4-$ as a function of initial concentration by Cs/Gltn/PDMAEMA, Cs/Gltn/PDMAEMA- treated and Cs/Gltn/PDMAEMA -SiO$_2$ composite, time;240 min, pH; 2, and adsorbent dose;2.5g/L.
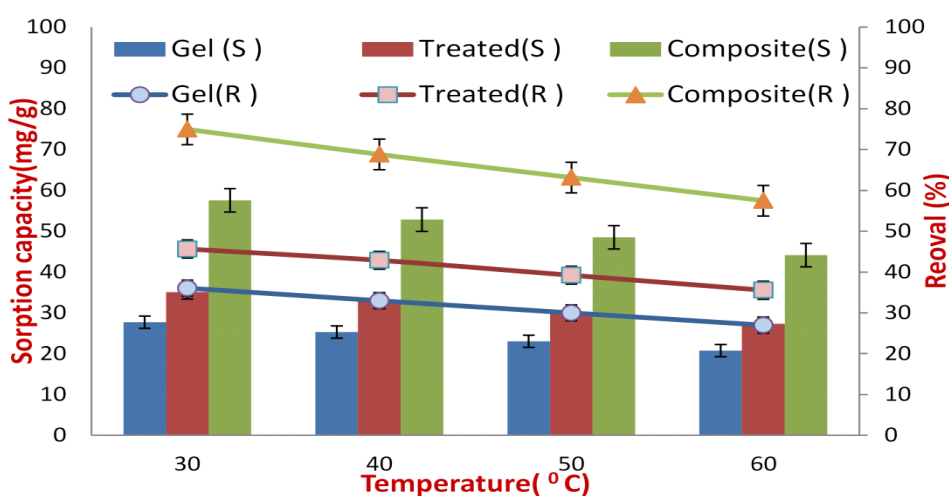

Fig. 7. The sorption capacity (S) and the removal percent (R) of H$_2$PO$_4-$ as a function of temperature by Cs/Gltn/ PDMAEMA, Cs/Gltn/PDMAEMA- treated and Cs/Gltn/PDMAEMA -SiO$_2$ composite, time; 240 min, initial concentration 192 mg/L, pH; 2, and adsorbent dose; 2.5 g/L.

pH dependency of the phosphate adsorption was related to both surface charge of the adsorbent and to the polyprotic nature of phosphate [27]. Figure 8 shows the effect of pH on the adsorption of phosphate ions. It can be observed that the removal of phosphate ion increased with increasing pH from 2 to 6 where the maximum removal was obtained. A decline in removal was done at pH 8. Since phosphate can exist in the form of H_3PO_4 at pH less than 2, $H_2PO_4^-$ at pH ranged between 2-7, HPO_4^{2-} at pH ranged between 7-12.5 and PO_4^{3-} at pH higher than 12.5[28]. With increasing pH from 2 up to 6 more di-hydrogen phosphate ($H_2PO_4^-$) existed in the solution which electro-statically attracted on the positive sites of - NH_3^+, - $NH_2^+(CH_3)_2$, -SH_2^+ and- Si-O^+H_2 on the surface of adsorbents [29-31]. The surface charge of CS is positive in acidic medium, gradually decreases with increasing in pH up to the zero point of charge at pH 6.4 [32]. When pH is equal or above 7, the surface becomes negatively charged due to the presence of -OH$^-$, -COO$^-$ groups which repels phosphate ions and hence decreased the affinity of phosphate to be adsorbed on the surface of adsorbents thus, the removal for phosphate decreased [33]. On the other hand, the removal of $H_2PO_4^-$ by the adsorbent systems are ordered in the sequence of Cs/Gltn/PDMAEMA/ SiO$_2$ composite > Cs/Gltn/PDMAEMA-treated > Cs/ Gltn/PDMAEMA hydrogel which revealed a higher number of functional groups and active sites. It can be explained by that in Cs/Gltn/PDMAEMA-SiO$_2$ composite the Si-O-Si bond on the surface generate

dipolar–dipole bond interaction with $H_2PO_4^-$ anions. This physical interaction enhanced the adsorption of $H_2PO_4^-$ by Cs/Gltn/PDMAEMA-SiO$_2$ composite compared with Cs/Gltn/PDMAEMA hydrogel as shown in Fig. 9.

Adsorption kinetic

In order to analyze the adsorption kinetics of adsorption of $H_2PO_4^-$ by Cs/ Gltn/P DMAEMA, Cs/ Gltn/ PDMAEMA- treated and Cs/ Gltn/ PDMAEMA/ SiO$_2$ composite Lagergren's equation or pseudo -first- order (Eq.1) and pseudo-second-order (Eq.2) kinetic rate models were applied [34]

$$\log (q_e - q_t) = \log q_e - \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 \, q_e^2} + \frac{1}{q_e} t \quad (2)$$

where q_e (mg/g) is the adsorption capacity at equilibrium and q_t (mg/g)) is the adsorption capacity at time t. k_1 (1/min) and k_2 (g/mg min) are the pseudo-first-order and pseudo-second-order rate constants,

The above kinetic models, (Eq.1) and (Eq.2), were used to fit the experimental kinetic data as shown in Fig. 10 and the data are summarized in Table 1. It can be observed that the pseudo-second-order model fitted well the experimental data. The correlation coefficients of the pseudo-second-order rate model are higher than the pseudo-second-order rate model for all investigated samples.
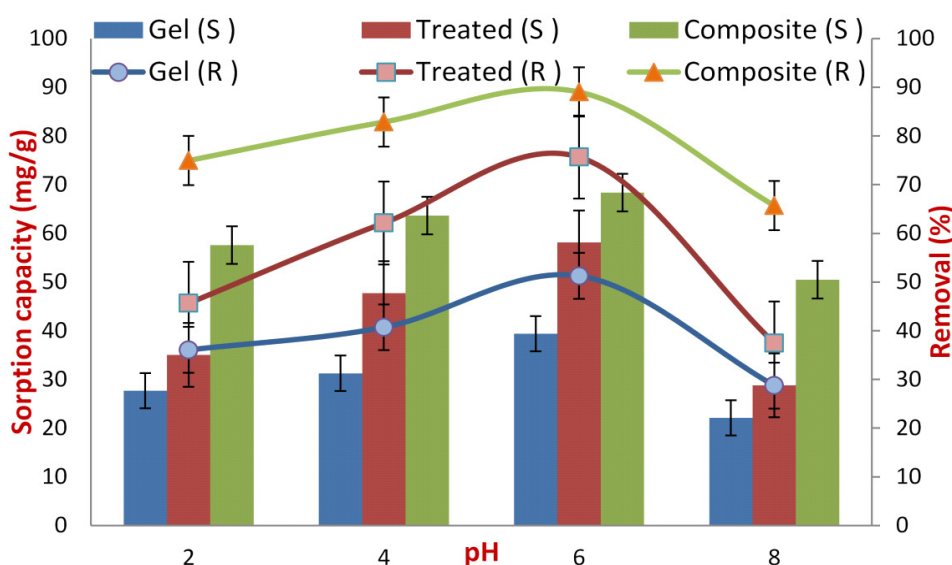

Fig. 8. The sorption capacity (S) and the removal percent (R) of $H_2PO_4^-$ as a function of pH by Cs/Gltn/ PDMAEMA, Cs/Gltn/PDMAEMA- treated and Cs/Gltn/PDMAEMA -SiO$_2$ composite, time; 240 min, initial concentration 192 mg/L, and adsorbent dose; 2.5 g/L.
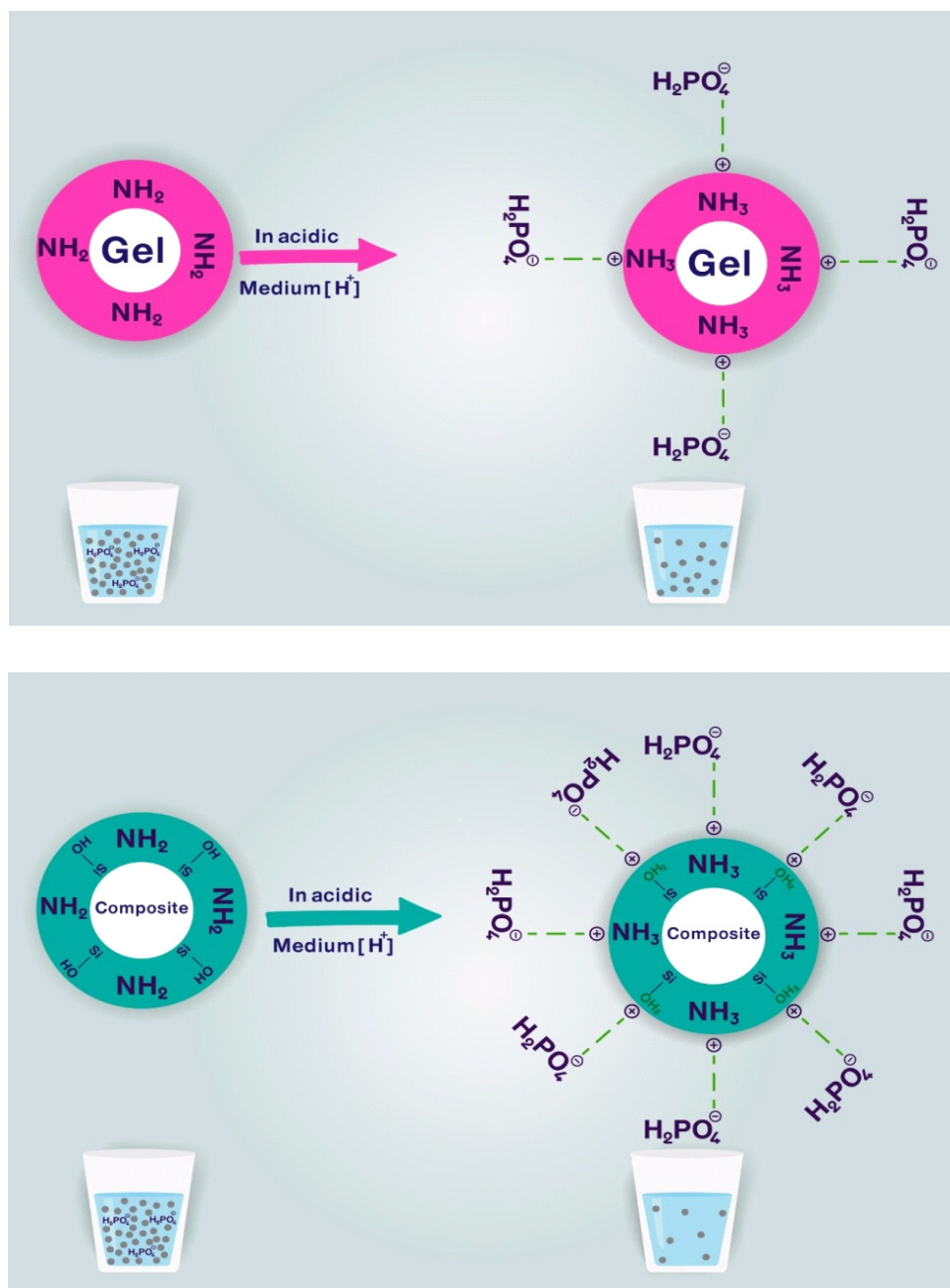
Fig. 9. A diagram presents the effect of presence of SiO$_2$ in Cs/Gltn/PDMAEMA-SiO$_2$ composite in adsorption of phosphate ions.

Adsorption Isotherm

The equilibrium adsorption data were analyzed by Langmuir (Eq.3) and Freundlich [35] (Eq.4) isotherm models

$$\frac{C_e}{q_e} = \frac{C_e}{qmax} + \frac{1}{b \, qmax} \qquad (3)$$

$$\ln q_e = \ln K_F + \frac{1}{n} ln C_e \qquad (4)$$

where C_e (mg/ L) is the equilibrium concentration of H$_2$PO$_4^-$ in the solution, b is the Langmuir constant (L/mg) that relates to the affinity of binding sites and q$_{max}$ is the theoretical saturation capacity of the monolayer (mg/g). K_F (L/g) is the Freundlich constant, and n is an empirical parameter that varies with the degree of heterogeneity and is related to the distribution of bonded ions on the sorbent surface.
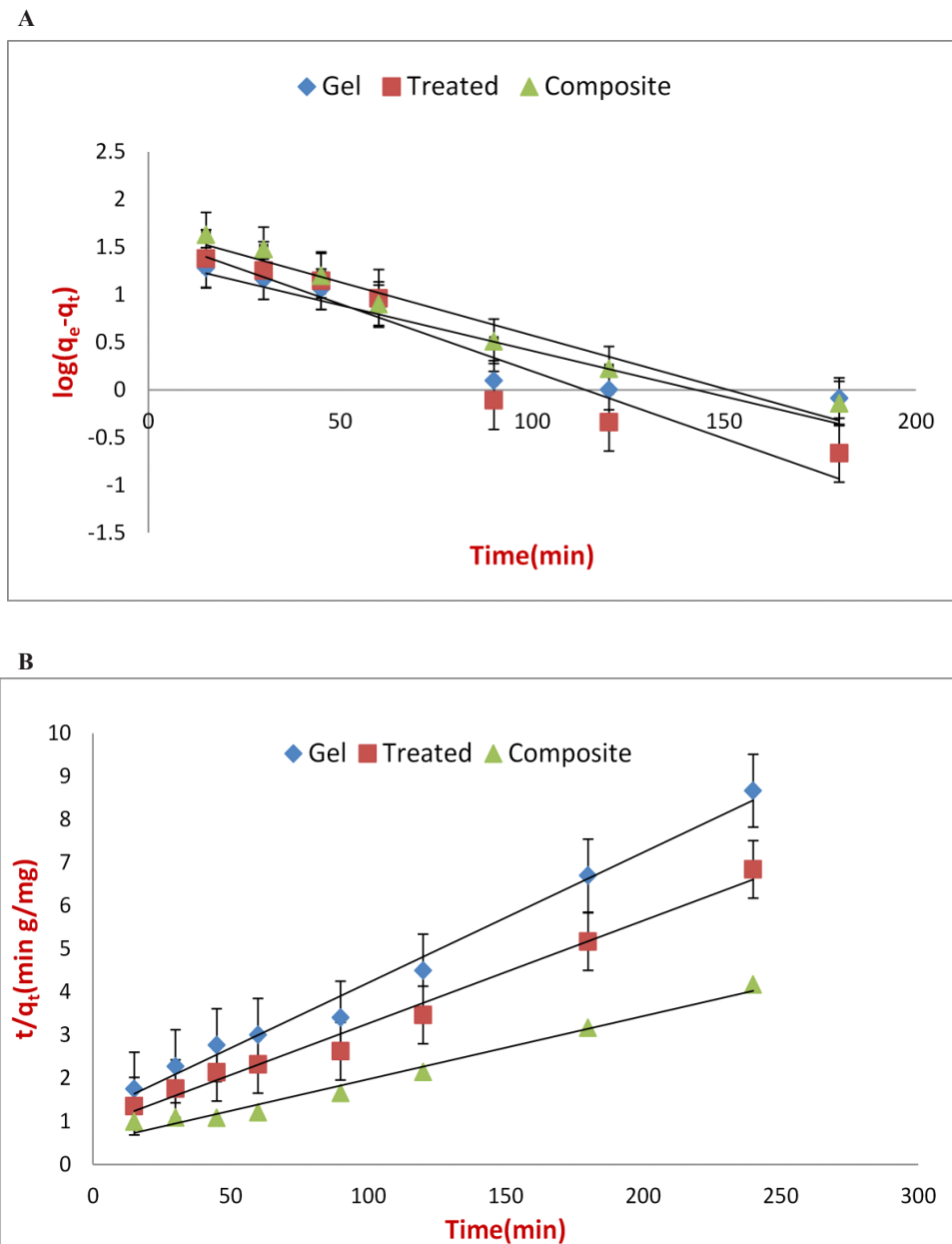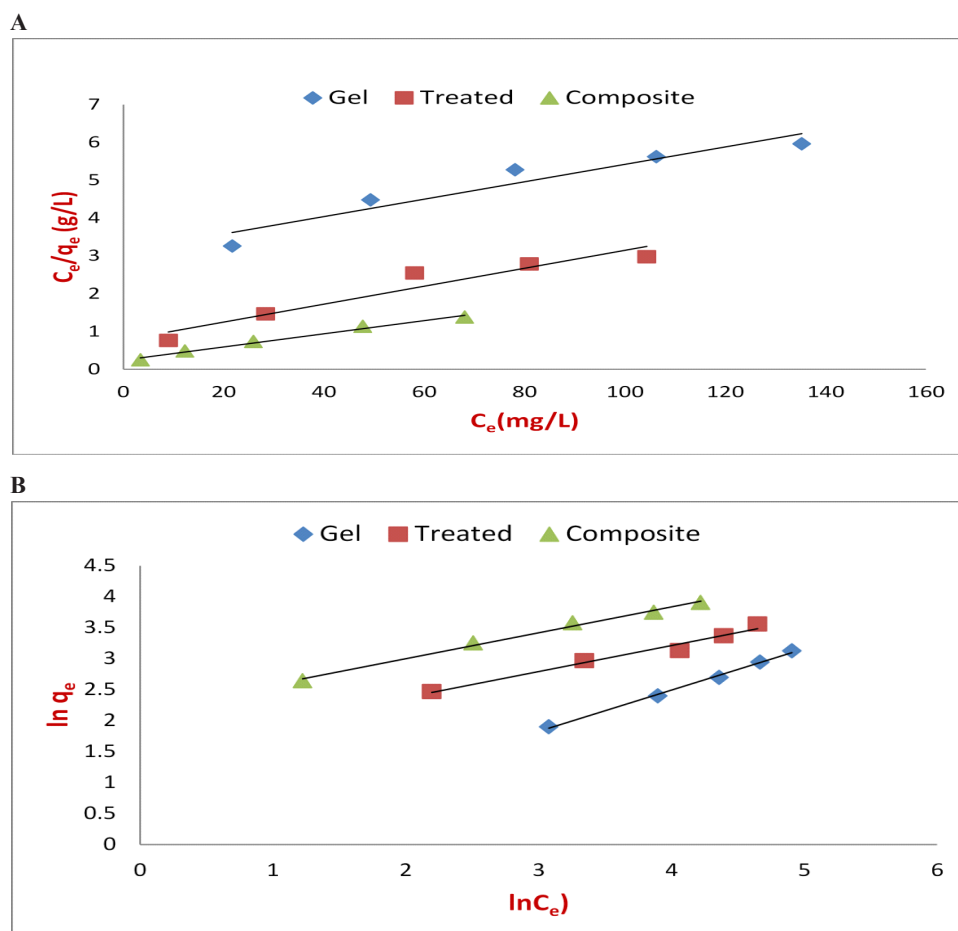
A

B

Fig. 10. Curves fitting of the pseudo-first-order (A) and Freundlich (B) adsorption isotherms for adsorption of $H_2PO_4^-$ by Cs/Gltn/PDMAEMA, Cs/Gltn/PDMAEMA-treated and Cs/Gltn/PDMAEMA -SiO$_2$ composite.

Figure 11 shows the isotherm plots of Langmuir and Freundlich models for adsorption of $H_2PO_4^-$ using Cs/Gltn/PDMAEMA, Cs/Gltn/PDMAEMA-treated and Cs/Gltn/PDMAEMA/SiO$_2$ composite and the isotherm models parameters were evaluated as shown in Table 1. It can be noted that the correlation coefficients (R^2) of the Freundlich isotherm model is higher than the Langmuir model for all investigated systems. This results indicated that the adsorption process mainly physical adsorption. Thus, the adsorption is heterogeneous energy distribution. It can be also noted that the values of n are higher than unity. The higher the n value the higher the heterogeneous the surface which indicating a favorable adsorption is done. Therefore, as seen in Table 1 Cs/Gltn/PDMAEMA/SiO$_2$ has the highest favorable for adsorption of $H_2PO_4^-$ and Cs/Gltn/PDMAEMA has the lowest one.

TABLE 1. Pseudo-first-order pseudo-second-order , Langmuir, and Freundlich models parameters for adsorption of H₂PO₄⁻ ions by Cs/Gltn/PDMAEMA, Cs/Gltn/PDMAEMA-treated and Cs/Gltn/PDMAEMA/SiO₂ composite.

Items	Gel	Treated	Composite
$q_{e,exp}$ (mg/g)	27.696	35.056	57.57
pseudo-first-order model			
R²	0.851	0.9062	0.9543
K_1 (min⁻¹)	-0.02211	-0.03247	-0.0257
$q_{e,cal}$ (mg/g)	23.2594	40.5415	48.8652
pseudo-second-order model			
R²	0.9874	0.9854	0.9795
k_2 (g.mg⁻¹min⁻¹)	0.000776	0.00064837	0.00042604
$q_{e,cal}$ (mg/g)	33.0033003	41.8410042	68.0272109
Langmuir model			
R²	0.9177	0.921	0.971
q_{max} ,cal (mg/g)	43.478	42.194	57.471
b (L/mg)	0.007	0.031	0.072
Freundlich model			
R²	0.997	0.974	0.987
n	1.502	2.387	2.825
K_F (mg/g)	0.841	4.628	12.178

Fig. 11. Curves fitting of Languimer (A) and Freundlich adsorption isotherms of H₂PO₄- by Cs/Gltn/PDMAEMA, Cs/Gltn/PDMAEMA-treated and Cs/Gltn/PDMAEMA -SiO₂ composite.

Conclusion

(Cs/Gltn/PDMAEMA) hydrogel was prepared by gamma irradiation. It was found that the gelation increases with increasing PDMAEMA content in the hydrogel. The maximum gel fraction was obtained at an equal ratio of Cs/Gltn at a radiation dose of 15 kGy. The modification of Cs/Gltn/PDMAEMA hydrogel with thiourea was done to increase the sorption capacity. Moreover, the incorporation of SiO_2 in the hydrogel was done to produce Cs/Gltn/PDMAEMA/SiO_2 composite. The adsorption capacities of the prepared systems towards phosphate ions were investigated. It was found that the removal percentage increases with the increase of the adsorbent dose while the adsorption capacity decreases. On the other hand, the removal percentage decreases by increasing $H_2PO_4^-$ ions' concentration and temperature. The maximum removal percentage was achieved at pH 6 within 180 min. The removal of $H_2PO_4^-$ by the adsorbent systems are arranged in the sequence of Cs/Gltn/PDMAEMA/SiO_2 composite > Cs/Gltn/PDMAEMA-treated > Cs/Gltn/PDMAEMA hydrogel. The pseudo second-order equation fits well the adsorption kinetics. The adsorption isotherm follows the Freundlich model higher than the Langmuir model.

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إزالة أيونات الفوسفات من المياة الملوثة بواسطة هيدروجيل معالج معتمد على الكيتوزان

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تم في هذا البحث تحضير هيدروجيل الكيتوزان/جيلاتين/-2(ثنائي ميثيل)إيثيل ميثأكريلات (Cs/Gltn/PDMAEMA) باستخدام التشعيع الجامي لإزالة أيونات الفوسفات من المياة الملوثة وقد تم معالجة الهيدروجيل بالثيويوريا لإدخال مجموعة الثيو للهيدروجيل المعالج Cs/Gltn/ PDMAEMA-treated كما تم أيضا إضافة SiO2 لتكوين متراكب Cs/Gltn/PDMAEMA/SiO2 حيث وجد ان نسبة الجلتنة تزداد بزيادة محتوى PDMAEMA في الهيدروجيل وأن أفضل جلتنة تحدث عند تساوى محتوى Cs/Gltn وعند جرعة إشعاعية 15 كيلوجراي. تم فحص قدرات الإمتزاز للأنظمة المعدة تجاه أيونات الفوسفات حيث تم الحصول على الحد الأقصى للإزالة عند درجة الحموضة 6 خلال فترة زمنية 180 دقيقة ولكن وجد أن نسبة الإزالة تقل مع زيادة تركيز أيونات الفوسفات ودرجة الحرارة, و وجد أن قدرة الممتزات المحضرة على إزالة أيونات الفوسفات مرتبة تصاعديا في تسلسل الأتي Cs/Gltn/PDMAEMA , Cs/Gltn/PDMAEMA-treated, Cs/Gltn/ PDMAEMA/SiO2 composite كما وجد ان حركية الامتزاز تتبع معادلة الدرجة الثانية الزائفة بشكل جيد وأن ايزوثرم الامتزاز يتبع نموذج فرندليش أعلى من نموذج لانجمير.