



Removal of copper (II) from aqueous solutions by sodium alginate/hydroxy apatite hydrogel modified by Zeolite

Afsaneh Barekat^{1*}, Masoomeh Mirzaei²

¹ Department of Chemistry, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

² Department of Chemical Engineering, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran

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ABSTRACT

The study presented in this article investigated the removal of copper ions from aqueous solutions by a synthetic hydrogel-forming adsorbent polymer based on sodium alginate (SA) and hydroxy apatite (HA) nanoparticles. The effect of adding Zeolite on the adsorption performance of this hydrogel was also investigated, and the optimum amount of Zeolite was determined by changing its quantity. The FTIR spectrum determined the structure of the synthesized adsorbent; non-continuous adsorption tests were performed to study the kinetics and thermodynamics of adsorption and also the recovery of the adsorbent. The degree of adsorption of the synthesized nanocomposite was compared with that of Zeolite, and the results showed that the maximum adsorption capacities of Zeolite and the nanocomposite for Cu ions were 29.7 and 75.8 mg/g, respectively. The kinetic studies indicated that the process of adsorption of Cu ions on both adsorbents followed a pseudo second order kinetic equation. It took the Zeolite and the hydrogel 90 and 120 minutes, respectively, to reach equilibrium. The thermodynamic studies showed that Cu adsorption by both adsorbents matched the Langmuir isotherm very well ($R^2=0.99$). Since adsorbent recovery and its lifespan are of significant importance in absorption processes, recovery was carried out by hydrochloric acid (2% by weight). The repulsion coefficient of the recovered adsorbent and its efficiency in five recovery cycles were measured. The results of the tests indicated that the repulsion coefficient of Cu was 70-82.75 percent and the adsorption efficiency of Cu after 5 recovery cycles was 75 percent of the initial adsorbent.

1. Introduction

At present, various sources of industrial wastewater, including that of petrochemical, paper and pesticide industries, tanneries, etc., contain impermissible amounts of heavy metals such as chromium, mercury, cadmium, lead, etc. The accumulation of these heavy metals has created a massive problem for microorganisms [1]. The human body needs Cu, but excess levels results in problematic conditions such as nervous disorders, various types of cancer, anemia, fatigue, nausea and vomiting, weakened immune system, etc. [2]. Researchers have introduced various methods including ion exchange,

electrochemical reactions, membrane filtration, and adsorption for removing and reducing heavy metals present in aqueous solutions. The cost and environmental effects of adsorbents are factors that must be considered in their selection. Adsorption has been widely used for water purification because it is an inexpensive and non-toxic method that is easy to design and implement [3-6]. Hydrogels are a class of polymeric materials with a three-dimensional network structure (physical or chemical cross-linking). In recent studies, hydrogels have exhibited very high adsorption capacities for removing pollutants such as heavy metals [7]. SA is a hydrophilic polysaccharide with an anionic nature, mainly composed of the cell walls of marine

*Corresponding author. Telephone: +98-9132944610

E-mail address: afsaneh.barekat@yahoo.com

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brown algae. This is an environmentally friendly/biodegradable and non-toxic natural polymer. The physical and chemical properties of alginates are directly related to their molecular structures. In 2016, Nichelle et al. produced hydrogels that were based on sodium alginate and used them to remove methylene blue dye. They performed continuous and discontinuous experiments, obtained the total pollutant adsorption in the column of 255.5 mg/g of the adsorbent, and the discontinuous experiments indicated that the adsorption data matched very well with Langmuir's isotherm [8]. Xiao et al. (2016) produced the SA adsorbent by adding graphene oxide nanoparticles and used it to adsorb heavy metals in discontinuous systems. SEM images showed that graphene oxide increased the porosity of the adsorbent; the adsorption tests indicated that the maximum adsorption of Cu and lead ions were 98 and 257 mg/g of the adsorbent, respectively [9]. Anne et al. (2015) studied the competitive adsorption of bivalent metal ions of metals such as Pb, Ni, Ca, and Cu by using hydrogel granules in continuous and discontinuous experiments. The kinetic experiments showed that 80 percent of the adsorption took place within four hours, equilibrium was reached in 48 hours, the adsorbent could be reused by using 4 percent hydrochloric acid, and the adsorbent could be recovered for nine times with 90 percent of its adsorption capacity [10]. K. Vijayalakshmi studied the use of biopolymer grains consisting of three nanochitosan adsorbents NCS/SA/microcrystal cellulose (MC) in a 1:8:2 ratio as an inexpensive adsorbent for removing Cu from aqueous solutions using the discontinuous method [11]; their laboratory results matched the pseudo second order kinetic model very well ($R^2=0.999$). The present research conducted a laboratory study of Cu removal from aqueous solutions by means of a synthetic hydrogel-forming adsorbent polymer based on SA/HA nanoparticles with the Zeolite additive and compared the performance of Zeolite and the synthesized hydrogel.

2. Theoretical relations

The parameter of adsorption capacity (mg/g) and adsorption percentage (R) are used in adsorption calculations using the following

$$q = \frac{C_0 - C_e}{m} \times V \quad (1)$$

where C_0 (ppm) and C_e are pollutant concentrations before and after the adsorption process, V is the volume of the solution in liters, and m is the mass of the hydrogel in mass units.

$$R = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where C_0 is the incoming concentration, C_e is the final concentration in mg/l, and R is the percent adsorption.

2.1. Pseudo first-order kinetic model

The linear form of the pseudo first-order kinetic model is as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

In the above relation, q_e and q_t are metal adsorption (mg/g) at equilibrium and at a given time t (min); k_1 is the kinetic constant of the pseudo first-order kinetic model.

2.2. Pseudo second-order kinetic model

The linear form of the pseudo second-order kinetic model is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

In the above relation, q_t (mg/g) is metal adsorption at time t (min), q_e is adsorption at equilibrium, and k_2 is the kinetic constant of the pseudo second-order kinetic model.

2.3. Langmuir's isotherm

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

In the relation above, the Langmuir constants q_m (mg/g) and K_L (L/mg) are related to the maximum single-layer adsorption and the adsorption energy, respectively. The larger the value of K_L , the greater the attraction between the adsorbed component and the adsorbent will be. Moreover, q_e (mg/g) and C_e (mg/L) represent adsorption at equilibrium and equilibrium concentration of the adsorbed component, respectively. The parameters of Langmuir's isotherm can be obtained by drawing its linear diagram:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b q_{max}} \quad (6)$$

As can be seen in relation 6, if the C_e/q_e line is drawn against C_e , the slope of the line and the y-intercept will be q_m and K_L , respectively.

2.4. Freundlich isotherm

$$q_e = K C_e^n \quad (7)$$

In relation 7, K is the Freundlich constant related to adsorption capacity; n (the Freundlich dimensionless constant related to the strength of adsorption) has a value between zero and one and the larger its value is, the greater the attractive forces between the adsorbent and the adsorbed component will be. The Freundlich constants (n and k) are related to adsorption intensity and adsorption capacity, respectively. The linear of the Freundlich isotherm is used to make the calculations easier. The linear form of

the Freundlich isotherm is derived as follows by taking the logarithm of relation 7:

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e \quad (8)$$

The constants in the Freundlich isotherm will be derived from the slope and the y-intercept of the linear diagram $\ln(q_e)$ against $\ln(C_e)$, as shown in relation 8.

3. Materials and methods

3.1. Materials and equipment

The SA and HA supplied by the Sigma-Aldrich Company, commercial Zeolite, and Cu sulfate pentahydrate, ammonia, and sodium chloride provided by the Merck Company were used together with a UV absorption spectrometer, model 7115, made by the JINWAY Company. Other equipment included a model DK203H ultrasonic instrument produced by the German Company BADDELIN and a RH b2 model magnetic heater made by the German Company IKA.

The phase analysis of fabricated framework was done by an X-ray Diffraction (XRD) diffractometer, model: Equinox 3000, Intel Co. The micrographs and elemental analysis were obtained from Field Emission Scanning Electron Microscopy (FE-SEM) model: Mira II, Tescan Co. and Energy Dispersive Spectroscopy (EDS) model: Mira II, Tescan Co. instruments. Ultrasonic bath, model: S 4000, Misonix Co. with output power: 600W was used in the preparation process.

3.2. Description of the experiment

The adsorbent was first synthesized. The adsorption experiments were then conducted to study the effects of contact time, initial concentration, and adsorbent recovery. The performance of Zeolite in removing Cu was compared with that of the hydrogel that was synthesized under identical conditions.

3.2.1. Adsorbent synthesis

First, 0.2g of HA was mixed with 50 ml of water and placed in the ultrasonic instrument for 15 minutes for the HA to

completely disperse in the water. Subsequently, 1.5g of SA were added to the mixture and placed on the mixer until a homogeneous gel mixture was formed. Various quantities of Zeolite in weight ratios of zero to 25 percent were then added to the mixture. Each of the obtained gels was injected into 0.1M calcium chloride, and the granules were placed in a saline solution for two hours in order for them to acquire their stable form; then, they were dried.

3.2.2. Contact time

The adsorbent Zeolite (0.1 g) and also the synthetic hydrogel SA (0.1g) were put in contact with 25 ml of 300 ppm Cu for periods from zero up to 150 minutes; the amount of the Cu in the solution after each contact time was measured.

3.2.3. The effect of initial concentration

Twenty five ml of each of 100 to 500 ppm Cu solutions were added to the adsorbent Zeolite (0.1g) and also the synthetic hydrogel SA (0.1g); the mixtures were placed on the magnetic mixer for 150 minutes. The solutions were then removed from the adsorbents and Cu contents of the solutions were measured.

3.2.4. Adsorbent recovery

The employed hydrogels were put in 2% hydrochloric acid in order for the repulsion process to take place and the adsorbent to be recovered. The recovered adsorbent was then washed several times with distilled water to remove the acid and for the adsorbent to become neutralized for reuse. This process was repeated five times. The following equation for the repulsion coefficient was used to study the efficiency of the recovered adsorbent and calculate the coefficient of adsorbent repulsion and adsorption percentage in the various recovery cycles of the adsorbent:

$$D\% = \left(\frac{\text{Weight of heavy metal (mg) repulsed by the hydrochloric acid}}{\text{Metal ions (mg) adsorbed on the adsorbent}} \right) \times 100 \quad (9)$$

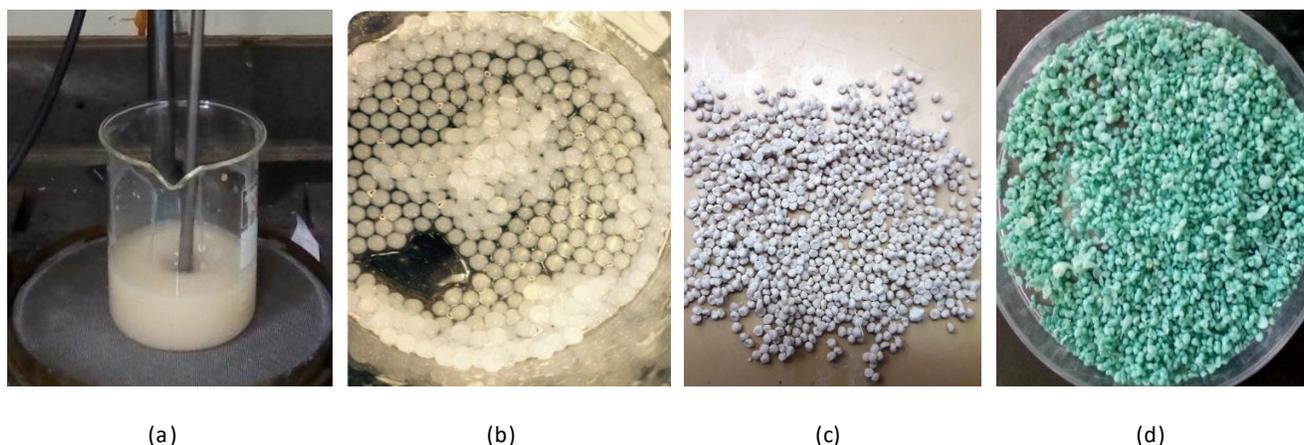


Fig. 1. Hydrogel synthesis process (a) prepared gel, (b) injected granules, (c) dried adsorbent beads, (d) hydrogels after Cu adsorption

4. Results and discussion

The results of the tests on adsorbent identification and on the effects of salinity, competitive ion, and adsorbent recovery are presented below:

4.1. Adsorbent identification

The FTIR tests were used to confirm the chemical structure of the hydrogels. Spectra 1 and 2 shown in Figures. 2 and 3 are those of the pure SA and the composite hydrogel, respectively.

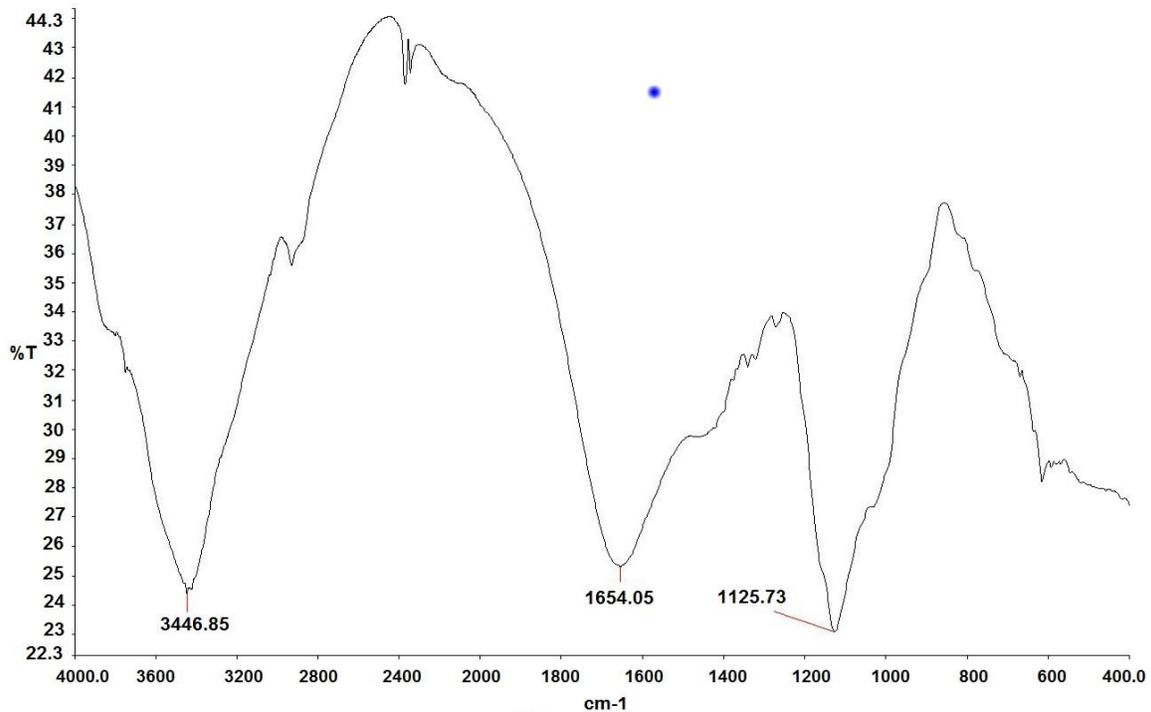


Fig. 2. FTIR spectra of pure sodium alginate

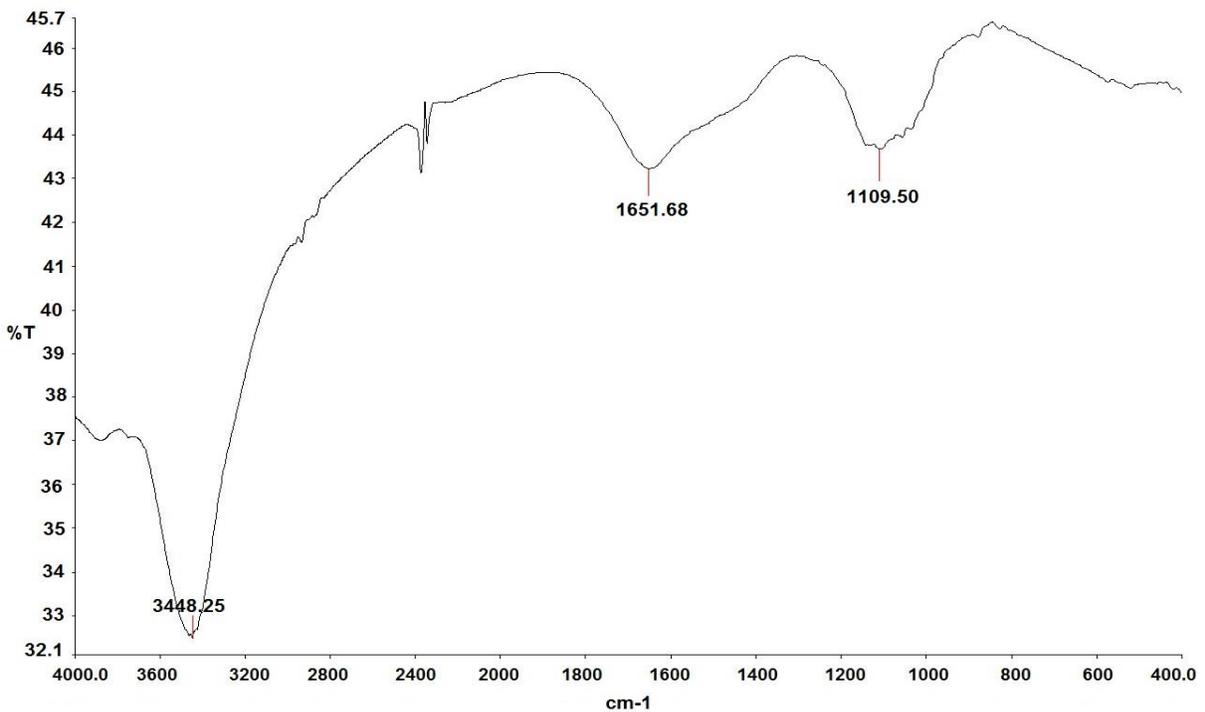


Fig. 3. FTIR spectra of synthesized hydrogel

Figure 2 displays the pure SA with peaks at 3448.25 cm^{-1} related to tensile vibrations of the hydroxyl group; at 1654.05 cm^{-1} to asymmetric tensile vibrations of the carboxylate group; and at 1125.73 cm^{-1} to tensile vibrations of the ether group in the polysaccharide. Figure 3 presents the composite hydrogel with a peak at 3448.25 cm^{-1} related to tensile vibrations of the hydroxyl group in the alginate chain, one at 1651.68 cm^{-1} to asymmetric vibrations of the functional carboxylate group, and another at 1109.50 cm^{-1} to vibrations of the C-O group. The adsorbent was produced in various weight ratios of Zeolite to SA (from zero to 25 percent). The adsorbent (0.1 g) was put in contact with 25 ml of a 300 ppm Cu solution for three hours. The results of this experiment are presented in Figure 4.

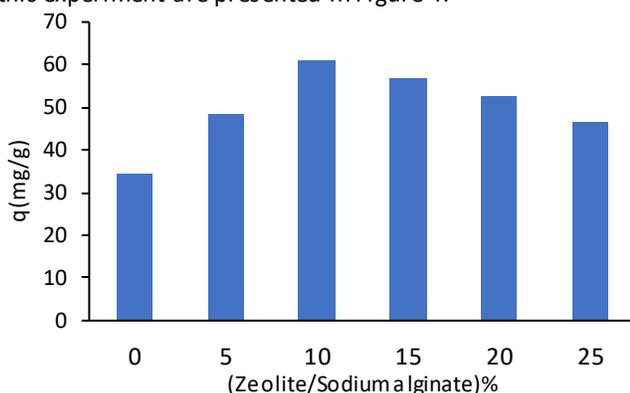


Fig. 4. Effect of Zeolite/Sodium alginate weight percent on adsorption capacity of hydrogel

As can be seen in Figure 4, the adsorption capacity of the hydrogel increased when the weight ratio of Zeolite was raised from zero to 10 percent. This could be due to the capacity of Zeolite in adsorbing Cu. In other words, the ability of Zeolite in adsorbing heavy metals in addition to the functional groups in the hydrogel increased the adsorption capacity. However, the adsorption capacity declined in samples with weight ratios of 15-25 percent because the porosity and swelling capability of the hydrogels in these samples decreased due to their high content of Zeolite. Therefore, we concluded that if clay and other mineral

additives were added to the hydrogel structure, their optimum ratios must be determined. The 10 percent weight ratio was selected for the synthesized hydrogel sample in this research.

4.2. Contact time

Adsorption experiments were carried out at various intervals for both Zeolite and the hydrogel to determine the related equilibrium times. The results are presented in Table 1.

The data related to the calculated capacities of Zeolite and the hydrogel for adsorbing Cu is plotted against time in Figure 5.

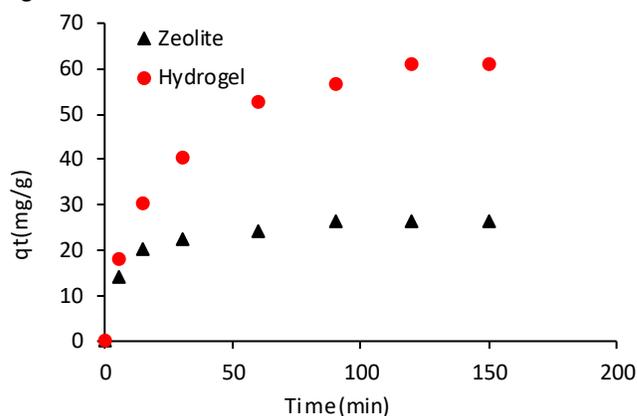


Fig. 5. Contact time effect for hydrogel and Zeolite

As shown in Table 1 and in Figure 5, the Zeolite achieved the maximum adsorption of 26.35 mg/g in 90 minutes, but the produced hydrogel reached equilibrium in 120 minutes and its maximum adsorption was 60.81 mg/g. The results showed that the Zeolite particles had a greater adsorption speed than the hydrogel granules. This could be due to the smaller size of the Zeolite particles and their greater surface area because Zeolite was used as a powder but the employed hydrogel had larger particles. However, it was observed that the adsorption capacity of the hydrogels was 2.3 times greater than that of the Zeolite.

Table 1. Experimental results of contact time effect for Zeolite and synthesized hydrogel

Hydrogel					Zeolite				
Time (min)	Ce (ppm)	Q (mg/g)	ln(qe-qt)	t/qt	Time (min)	Ce (ppm)	Q (mg/g)	ln(qe-qt)	t/qt
0	300	0			0	300	0		
5	227/02	18/24	3/75	0/27	5	243/24	14/18	2/49	0/35
15	178/37	30/40	3/41	0/49	15	218/91	20/27	1/80	0/74
30	137/83	40/54	3/00	0/74	30	210/81	22/29	1/40	1/34
60	89/18	52/70	2/09	1/13	60	202/70	24/32	0/71	2/46
90	72/97	56/75	1/40	1/58	90	194/59	26/35	-4/75	3/41
120	56/75	60/81	-4/68	1/97	120	194/59	26/35	-4/70	4/55
150	56/75	60/81	-4/68	2/46					

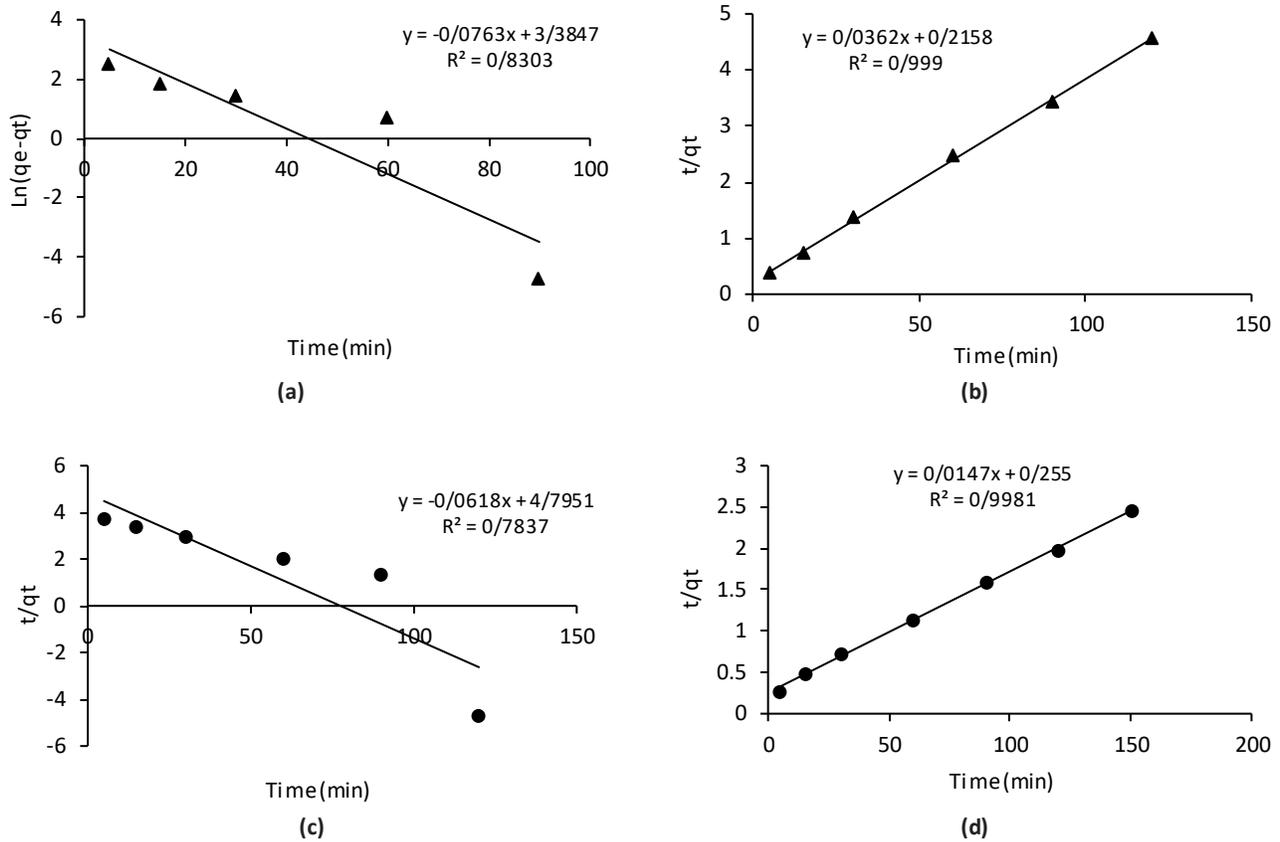


Fig. 6. Kinetics models (a) Pseudo first order for Zeolite, (b) Pseudo first order for hydrogel, (c) Pseudo second order for Zeolite, (d) Pseudo second order for hydrogel

In Table 1, the values of $\ln(q_e - q_t)$ and of t/q_t were calculated for drawing and studying the pseudo first and second order kinetic curves. In Figure 6, these values were plotted against time for both of the adsorbents. After drawing the kinetic curves, the constants of these equations were also calculated. The calculated values are listed in Table 2. The results showed that the pseudo second order kinetic curves for both adsorbents matched the empirical data very well.

4.3. Initial adsorbent concentration

Adsorption experiments were performed at various initial concentrations in the 100-500 ppm range to obtain the isotherm. The results are presented in Table 3.

The results indicated that the maximum adsorption of Cu was 29.71 mg/g for Zeolite and 75.82 mg/g for the hydrogel. Therefore, the synthetic hydrogel had a greater adsorption capacity than the Zeolite under identical conditions, concentration and the amount of the adsorbent. Using the results in Table 3, the Freundlich and Langmuir isotherm curves were drawn for both the Zeolite and the hydrogel (Figure 7) and their constants were calculated; they are listed in Table 4. The results showed that both adsorbents followed the Langmuir model.

Table 2. Kinetic models constants for hydrogel and Zeolite

Kinetic model order	Hydrogel			Zeolite		
	q_e (mg/g)	K (1/min)	R ²	Q_e (mg/g)	K (g/mg)	R ²
Pseudo first	120.3	0.062	0.783	29.38	0.076	0.830
Pseudo second	68.03	0.00084	0.998	27.62	0.006	0.999

Table 3. Experimental effect of initial concentration effect for hydrogel and Zeolite

Hydrogel						Zeolite				
C ₀ (ppm)	C _e (ppm)	q (mg/g)	Log (C _e)	Log (q _e)	C _e /q _e	C _e (ppm)	q (mg/g)	Log (C _e)	Log (q _e)	C _e /q _e
100	3/8	24/0	0/59	1/38	0/16	15	21/15	1/19	1/33	0/73
200	8	48/0	0/90	1/68	0/17	104	24/00	2/02	1/38	4/33
300	56	60/8	1/75	1/78	0/93	186	28/37	2/27	1/45	6/57
400	130	67/3	2/12	1/83	1/94	281	29/59	2/45	1/47	9/52
500	196	75/8	2/29	1/88	2/59	381	29/71	2/58	1/47	12/83

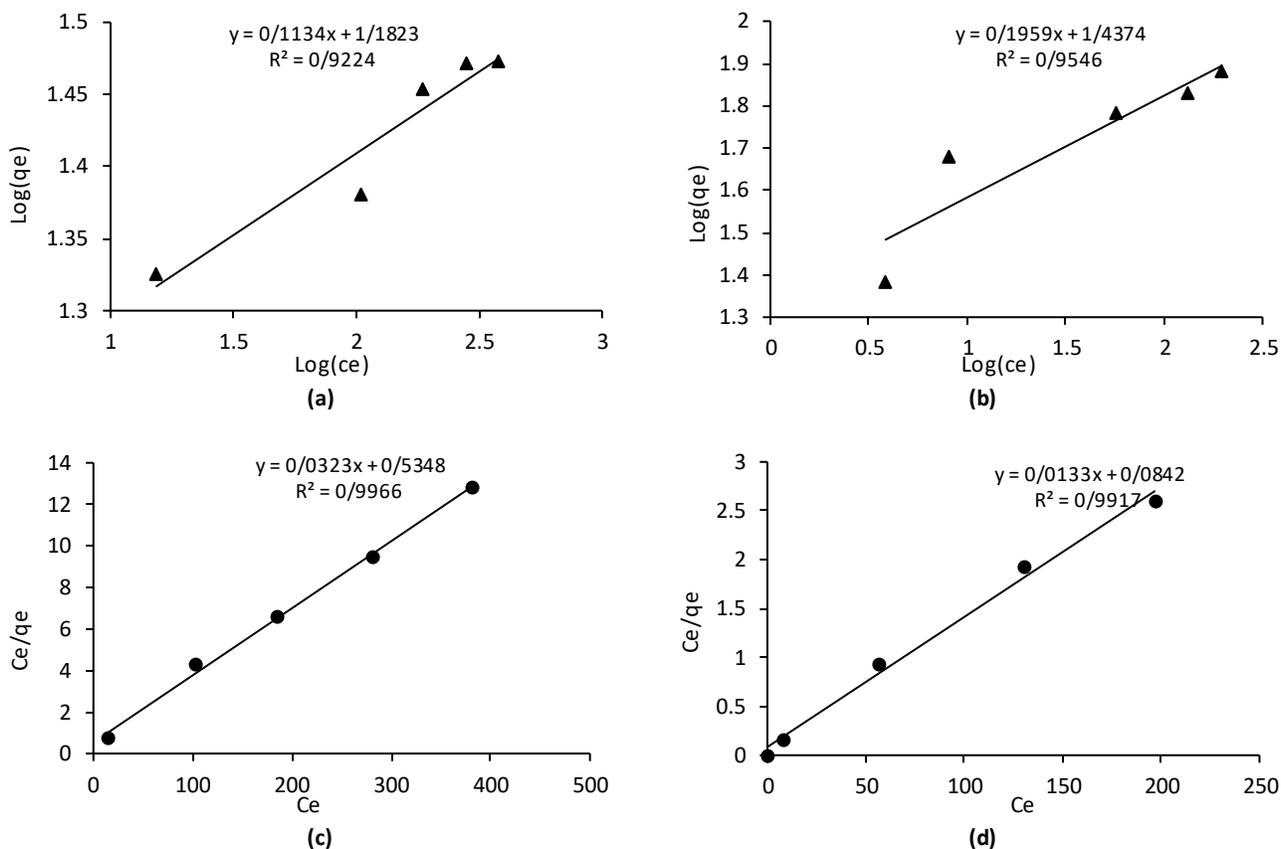


Fig. 7. Linear form of isotherms (a) Freundlich for Zeolite, (b) Freundlich for hydrogel, (c) Langmuir for Zeolite, (d) Langmuir for hydrogel.

Table 4. Thermodynamic constants of Freundlich and Langmuir isotherms for Zeolite and hydrogel

Langmuir			Freundlich			
q _m (mg/g)	K _L	R ²	n	K _f	R ²	
30.96	0.061	0.996	0.113	15.2	0.922	Zeolite
75.18	0.158	0.991	0.196	27.5	0.955	Hydrogel

4.4. Adsorbent recovery

The synthesized adsorbents were recovered after performing one stage of the process and were used in four successive stages. The table below shows the amounts adsorbed by the unused adsorbents and the quantities of

the recovered adsorbents. As shown in Table 5, the efficiency of the adsorption process using recovered adsorbents for five consecutive adsorption stages remained at about 75 percent, which shows a good capability in recovering the adsorbent and in reusing it. Formula 9 shows

that the adsorbent recovered by 2 percent of HCl had the repulsion coefficient of 70-82.75 percent.

Table 5. Comparison of fresh and reduced adsorbent

Recovery cycle no.	Removal %
Fresh adsorbent	81/2
1	77/4
2	72/1
3	66/5
4	61/2

5. Conclusions

The SA and Zeolite synthesized hydrogel had an adsorption capacity of about 2.3 times greater than that of Zeolite so that under identical conditions in regard to the amount of adsorbent and initial concentration, the adsorption capacity of Zeolite was 29.7 mg/g of the adsorbent and that of the hydrogel was 75.8 mg/g. The kinetic studies showed that Cu adsorption on the SA hydrogel and activated carbon followed the linear form of the pseudo second order model with $R^2=0.991$. The thermodynamic studies for determining the isotherm indicated that the laboratory data for both adsorbents matched with the Langmuir isotherm very well. The synthesized hydrogel had greater adsorption capacity but lower adsorption speed so that the equilibrium time was 90 minutes for Zeolite and 120 minutes for the hydrogel. It was possible to recover and reuse the adsorbent five times with the efficiency of 75 percent, and the repulsion coefficient of the adsorbent was 70-82.75 percent.

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