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Preparation and Properties of a Novel Eco-friendly Carboxymethylcellulose /K- Carrageenan /Graphene oxide Gel Beads for the Removal of Heavy Metals from Water

Manal El Hefnawy[1] K.A.Ali[2] M. M. Deef Allah[1]
1.Natural Science Department, Faculty of Engineering, Benha University, shoubra, Egypt
2.Applied Organic Chemistry Department, National Research Centre, Dokki, Giza 12622, Egypt

Abstract:
A novel environmentally-friendly adsorbents, carboxymethyl cellulose /k-carrageenan /graphene oxide (CMC/KC/GO) gel beads (GBs) was prepared via a simple method. The composition and morphology of these gel beads were characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis, and scanning electron microscopy. The maximum adsorption capacity of (CMC/KC/GO) GBs for Cu (II) and Co (II) was 2.85 and 1.87 mmol/g respectively at 30°C. Factors affecting the adsorption capacity of metal ions such as CMC/KC ratios, GO ratios, pH, initial metal ions concentration, and the temperature were also explored. The kinetics studies showed that the adsorption process followed the pseudo-second-order kinetics. The analysis of the isotherm indicated that the Langmuir isotherm is in a good agreement with the sorption process. The thermodynamic parameters indicate that the adsorption process was endothermic and spontaneous. The adsorption capacity of the GBs barely declined even after six cycles of regeneration; furthermore, the GBs can be simply separated from the aqueous solution after adsorption by a simple filtration.

Keywords: Carboxymethyl cellulose; k-carrageenan ;graphene oxide ; gel beads; isotherm

1. Introduction

The pollution of water resources by industrial effluents containing poisonous metal ions is one of the most serious problems nowadays, with the increased industrial development particularly in developing countries. Lots of heavy metals in the wastewater are being directly or indirectly discharged into the environment more and more every day. Moreover, heavy metals are not biodegradable and tend to accumulate in living organisms in addition of being toxic or carcinogenic. Toxic heavy metals of particular concern in the treatment of industrial wastewaters include copper, cobalt, nickel, lead, cadmium, and zinc. Although copper does essential work in animal metabolism, its excessive ingestion can lead to serious toxicological issues. [1]. Cobalt also is a very dangerous heavy metal; as its ions reach the food and water they cannot be destroyed and once the body is exposed to this metal, it can cause oxidative stress, DNA damage, and serious degenerative sickness. That's why now patients with hip implants containing Cobalt are suffering from tinnitus, deafness, vertigo, and blindness [2].

One of the most effective and economical methods for the treatment of heavy metals in wastewater is adsorption due to its flexible design and operation and high quality treated effluent, in addition to being reversible by suitable desorption process adsorbents can be regenerated. The development of natural, cheap, biocompatible and biodegradable polymer sorbents [3] is an extraordinary growing field in adsorbent materials research; as sorbents based on synthetic polymers are highly expensive with many difficulties in their regeneration. Many polysaccharides such as alginate, chitin, cellulose, chitosan and carrageenan have been widely used in water treatment. [4-6].Recently, researchers have been developing polymeric hydrogel beads containing various functional groups in its molecular structures as the most promising adsorbents materials for dyes molecules and heavy metal ions .These beads have adequate mechanical stability, specific large surface area, uniform shape and particle size[7,8]. One of these beads is CMC which has been effectively used in wastewater treatment processes due to its structure containing carboxylic group in it. However, purely cross-linked carboxymethylcellulose (CMC)beads have a weak mechanical stability and limited swelling degree; that's why it needs to be modified via blending [9],grafting [10],forming an interpenetrating network(IPN)and composite with other polymers .Similar to CMC carrageenan as a natural linear water soluble sulfated polysaccharide has been used in water treatment , due to its certain adsorption ability, in addition to being non toxic, and biodegradable [12,13], moreover, K-Carrageenan can also form gel beads similar to alginate and chitosan[14,15]. Currently, bio-based materials and carbon adsorbents are widely used to remove water pollutants [4,16] , as a carbon adsorbents, graphene oxide(GO) has shown excellent adsorption ability in removing organic and inorganic molecules due to its large surface area and the large amounts of functional groups like epoxy , hydroxyl, and carboxyl groups existed within its skeleton[17],it is considered a desirable material for enhancing the adsorption performance of hydrogel materials, and great efforts have been made to exploring the capability of GO based hydrogel materials for water treatments [18-20]. In view of the above data, it is reasonable to combine bio-based materials and carbon adsorbents to produce new adsorbents with higher adsorption ability.

In this study carboxymethylcellulose/k-carrageenan/graphene oxide gel beads (CMC/KC/GO) GBs were prepared by a simple method and have been used as an adsorbent for the removal of Cu (II) ions and Co (II) ions from aqueous solution. For this aim, thermal stability, adsorption capacities, adsorption kinetics and adsorption isotherm of the beads were investigated and, these beads were used after the regeneration process.

2. Experimental

Materials

Carboxymethylcellulose,k-carrageenan and graphite powdered (8000mesh) were purchased from Sigma Aldrich (Germany)KCl and $FeCl_3$were purchased from Park Scientific Limited U.K. all other reagents were of analytical grade and used as received .Distilled water was used in all experiments.

Preparation of composite beads

CMC and KC biopolymer solution were prepared by dissolving each of them separately in distilled water at 50°C for CMC and 70°C for KC under a mechanical stirring for 1hr. To prepare CMC/KC GBs different weight ratio (2:1,1.5:0.5,1:1,0.5:1.5,0:2)w/w were mixed together in distilled water at 70°C to have a final concentration 2% w/v for both biopolymer. GO was synthesized from graphite powder using a modified Hummer method [21, 22] then, a known amount of GO (0-0.8 %) was dissolved in distilled water at 70 °C for 15 min then added to the polymer solution with continuous stirring at the same temperature for another 30 min. The mixture was sonicated at the same temperature for another 15 min to obtain a homogenous solution, after the solution temperature decrease to 40°Cdropping it using a fine glass syringe into the gelling salt solution (3% $FeCl_3$ and 3% KCl) while the gelling salt solution in case of KC was only 3% KCl and in case of CMC only was 3% $FeCl_3$.After complete gelation (2h)the resultant spherical beads were collected by filtration and washed several times with distilled water and left to dry at room temperature for constant weight. The CMC/KC beads without GO were prepared by a similar method.

Characterization Techniques:

The chemical structure of the developed samples were analyze by the Fourier transform infrared spectroscopy (FTIR-Shimadzu 8201 PC in the range of 400- 4000 cm^{-1}in KBr phase, their thermal degradation behaviors were studied using thermal gravimetric analysis analyzer (TGA, Model 50/50 H, Shimadzu Japan) also, the surface morphology for the developed composite beads were investigated using scanning electron microscopy (SEM, Hitachi limited Japan)

Adsorption experiments

The removal of the heavy metals Cu (II) and Co (II) was accomplished using batch adsorption experiments at different conditions including, the ratio of CMC/KC in GBs the GO weight ratio, the influence of pH, contact time and temperature were carried out using 0.5 gm of beads in 25 ml of single metal ion solution in a controlled water bath shaker at 50 rpm and 30°C(except the effect of temperature).The sample was filtered to remove the beads and the concentration of the metal ions in the filtrate was measured using Hitachi atomic absorption Z-6100 polarized Zeeman. Experiments are carried out three times and the average value is presented. The capacity of adsorption q_e in the equilibrium (mmol/g) was calculated by the next equation

$$q = \frac{(C_o - C_e)V}{W} \qquad (1)$$

Where, C_o and C_e are the initial and final concentration of the metal ion V volume of the metal ion solution (L) and W is the weight of the dry GBs in (g).

3. Results and discussion

Beads characterization:-

FTIR spectra for native CMC, KC,GO, CMC/KC, and CMC/KC/GO composite beads were shown in fig 1 CMC spectra showed a broad absorption bands at 3424 $cm^{-1}$and 2920 cm^{-1} due to the stretching frequency of the O-H and C-H besides, broad symmetrical and asymmetrical vibrations at 1420 $cm^{-1}$and 1639cm^{-1} for the stretching of the carboxylate anions. The bands at 1068 and 1326 were assigned to sugar ring absorption and O-H bending vibration respectively. Compared with the spectra of CMC the same peaks in KC spectra not only appeared but also the basic characteristics function groups where ,the bands at 1380 cm^{-1} ,1261, 925cm^{-1},850cm^{-1}in KC spectra were attributed to the presence of sulphate groups and corresponding to the sulphonic acid groups, C-O stretching 3,6-anhydro D-glucose and glycosidic linkage of KC backbone respectively .The bands at 1068 and 1639 cm^{-1} in GO spectra are attributed to C-O and C=C stretching vibration[23] for CMC/KC/GO beads and CMC/KC beads the spectra did not vary much when GO encapsulating within the beads this could be due to the very low concentration of GO and IR spectrum of GO is covered by that of CMC/KC beads.

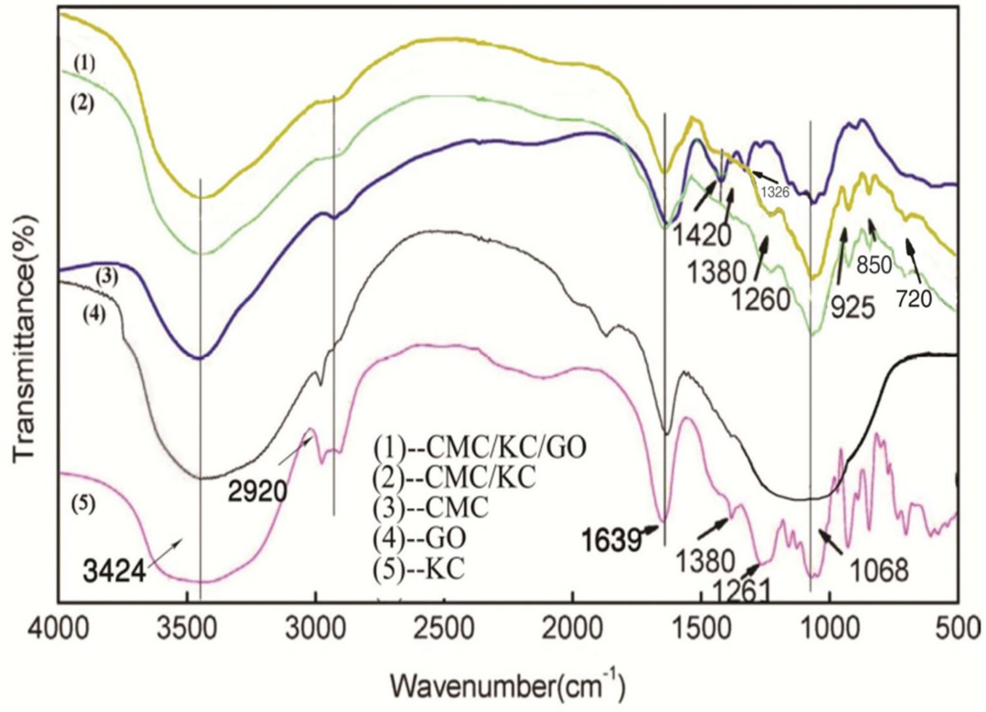


Figure 1. FTIR of CMC, KC, CMC/KC, CMC/KC/GO GB$_S$, and GO

Thermal stability of the prepared beads was studied by thermal gravimetric analysis, it was shown from Fig 2 that for GO the apparent weight loss in the range 25-190 is attributed to the loss of hydrated water while the significant weight loss 75% occurred in the range 185-230 as a results to pyrolysis of the labile oxygen functional groups and release of steam, carbon monoxide and carbon dioxide [24]. The apparent weight loss 0-150^{0}C in CMC and KC may be due to the loss of the moisture contents of CMC and KC, with increasing temperature the rate of weight loss increased and both second and third degradation stages took place. The observed weight loss beyond 200^{0}C could be related to the released of water more firmly bound through the polar interaction with COOH group in CMC and sulphate group in KC in addition to the loss of CO_2 as a result of decomposition of cyclic product in KC and CMC. On the other hand CMC/KC/GO GBs were found to be more thermally stable with increasing temperature and the temperature required to loss its half weight is 450^{0}C Compared to 310,400,388 for CMC,KC and CMC/KC beads.

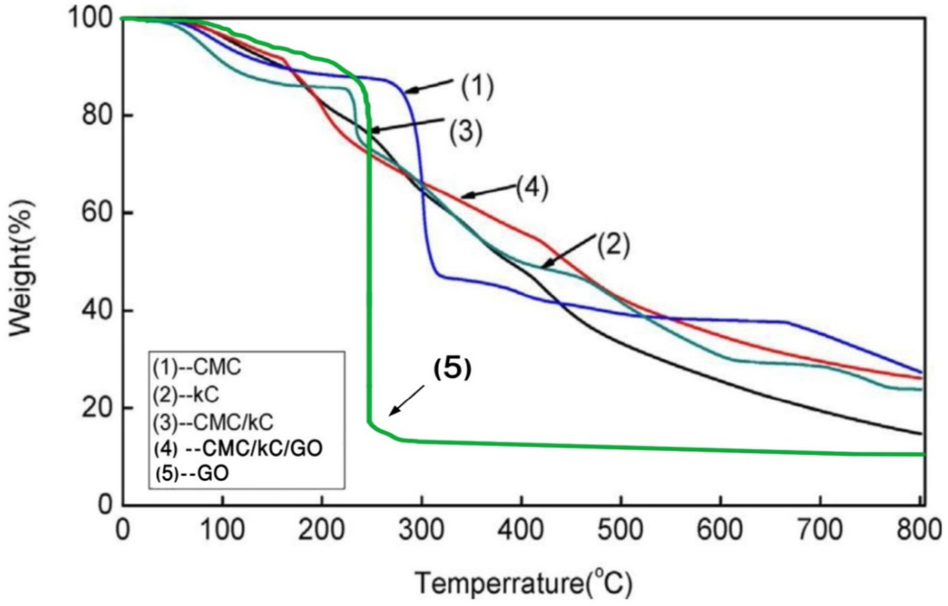
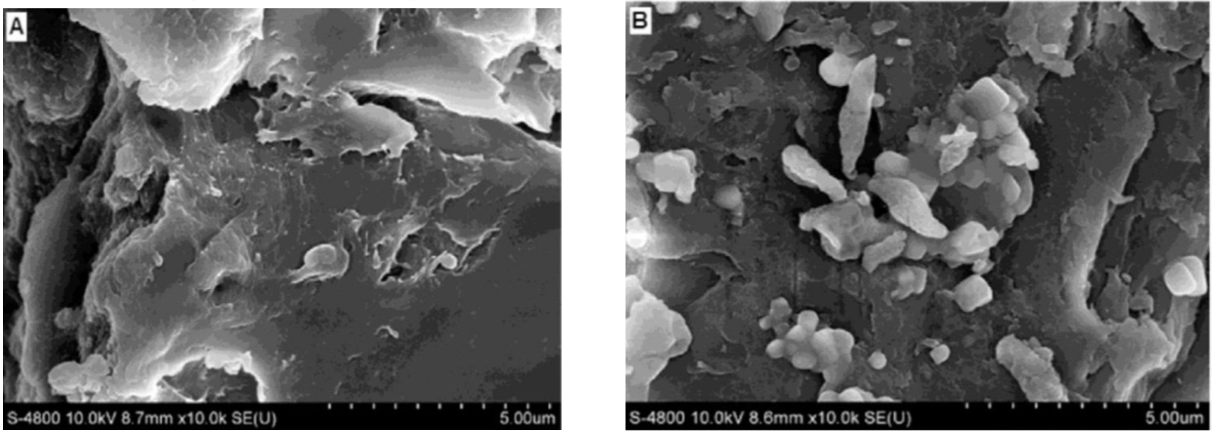
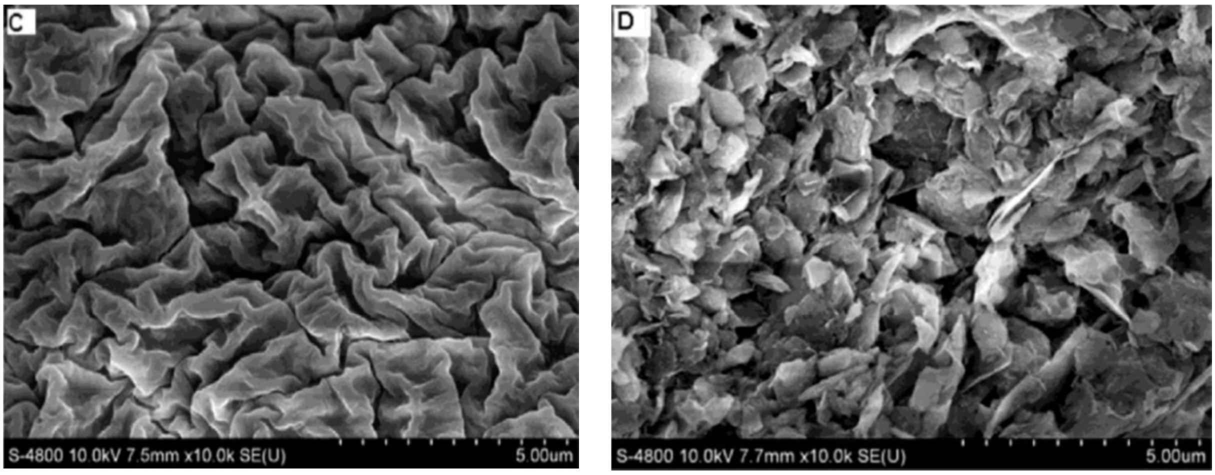


Figure 2. TGA carves of GO, CMC, KC, CMC/KC, and CMC/KC/GO GB$_S$

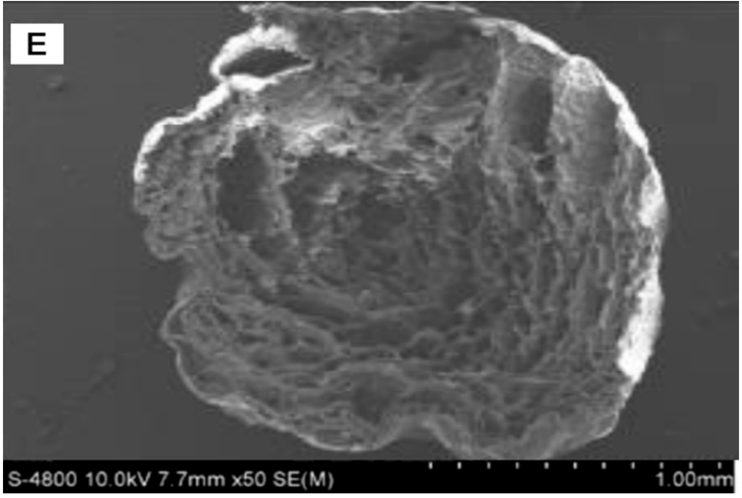
The morphological structure of the surface of the beads was investigated in Fig 3. It can be seen from fig3Aand 3B that CMC and KC beads were exhibited irregular fracture surfaces while in Fig 3C the CMC/KC beads surface was changed to a curly texture surface. Furthermore, CMC/KC/GO bead depicts a crusty and coarse surface as shown in Fig 3D also the pores and wrinkles become smaller and denser with the incorporation of GO, that supplying bigger specific surface which more suitable to adsorb metals ions. At low magnification value for the image of CMC/KC/GO GBs Fig 3E it was observed that the surface of it was not completely spherical and roughly due to the incorporation of GO with CMC/KC matrix



CMC GB$_S$ KC GBs



CMC/KC GB$_s$ CMC/KC/GO GB$_S$



CMC/KC/GO GB$_S$ (E) at low magnification
Figure 3. SEM of the prepared gel beads

Factors affecting metal ion adsorption

Effect of CMC/KC ratio

The effect of CMC/KC ratio at a different mass ratio and at a constant other adsorption condition was clarified in Fig 4 .Results showed that q_e mmol/g for all studied ratio increased gradually with increasing contact time from 30 min to 210 min. also, the beads containing both CMC/KC showed high q_e value than that for individual CMC and KC beads. CMC/KC ratio 1:1 record the highest q_e value for Cu (II) and reached 2.66 mmol/g after 180 min. from contact time these results indicated that the presence of CMC/KC with an equal ratio increases the exposed surface area with a large number of active site for further metal ion uptake. According to these results, the following factors affecting the metal uptake were studied based on CMC/KC (1:1) ratio in gel beads.

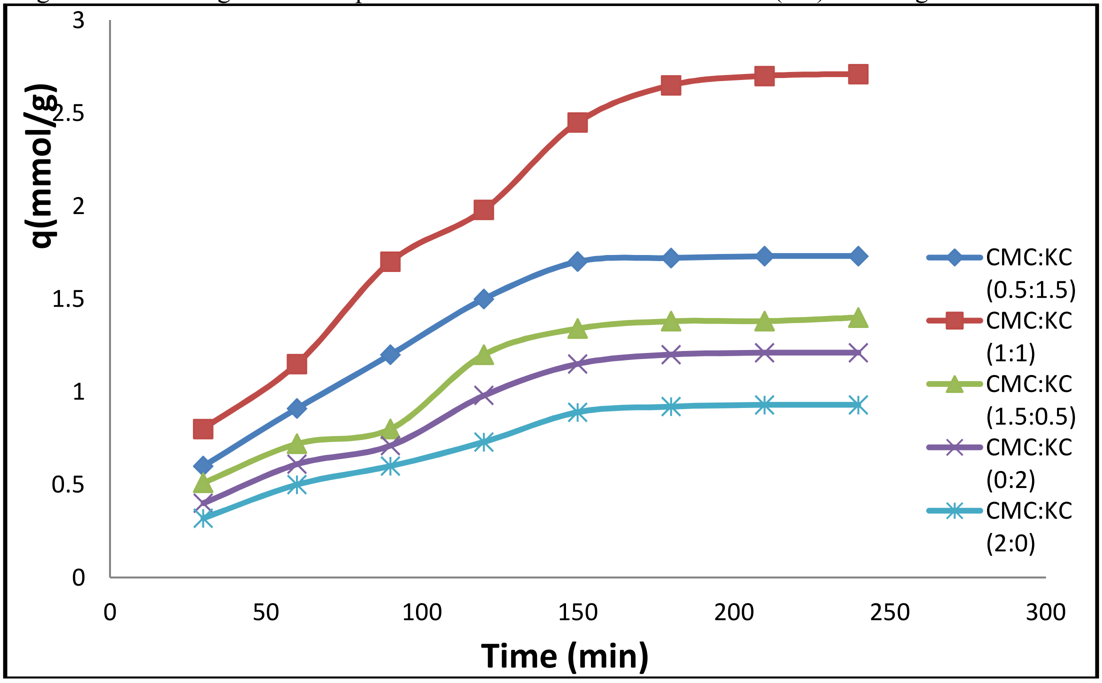


Figure 4. Effect of CMC/KC ratio on the adsorption capacity of Cu(II)at (0.6%)GO, adsorbent dosage(0.5g),metal ion(5mmol/L), solution temperature 30^{o}C,pH = 6and agitation speed (50rpm)

Effect of graphene oxide amount

It was observed from Fig 5 that the addition of GO improved the metal adsorption capacity compared to the free GO GBs at a constant mass ratio of CMC/KC 1:1 and other adsorptive condition. This mainly attributed to the interaction between CMC/KC/GO beads and the metal ions, as well as the porous internal structure of the beads. CMC/KC/GO GBs have smaller and denser pores than CMC/KC GBs which is beneficial to adsorb metal ion.

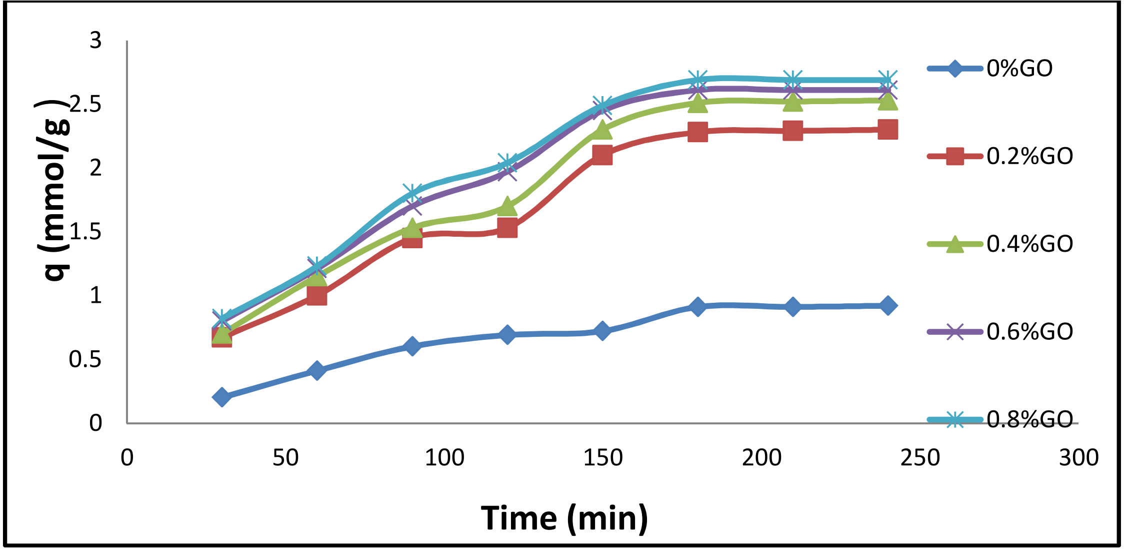


Figure 5. Effect of GO amount at constant CMC/KC (1:1) at 30^{o}C, metal ion concentration (5mmol/L), adsorbent dosage (0.5g) ,pH =6,and agitation speed=50rpm

Optimum pH of metal ions uptake

The optimum pH for sorption of Cu (II) and Co (II) ions was determined by shaking 0.5 gm of the dry beads (CMC:KC:GO 1:1: 0.8 %GO) with 25ml of metal ion solution (5mmol/L) for 3 h at 30°C in the pH range 1to7.It was observed from Fig 6 that the adsorptive capacity of the metal ions enhanced as the pH increased hence the gel beads have negative charge in solution due to the sulphate groups in KC and a abundant oxygen containing groups in graphene oxide [13,25],also with the increase of pH value most of the carboxylate groups of CMC are ionized to carboxylate anions COO^- where as pK_a for carboxylic groups is 4.5 so the amounts of negatively charged sites increases ,which increased the electrostatic interaction between these sites and the cations of the metal ions[26].The decrease in the adsorption capacity at lower pH may be due to the protonation of active sites such as carboxylates and hydroxyls hence the protonated hydrogen ions H^+ competes with the Cu(II) and Co(II) for free active sites of the GBs. The optimum pH value for Cu (II) and Co (II) was 5.6 and 6.1 respectively. After this value there is no high adsorption efficiency owing to the precipitation for all metal ions as metal (II) hydroxide [27].

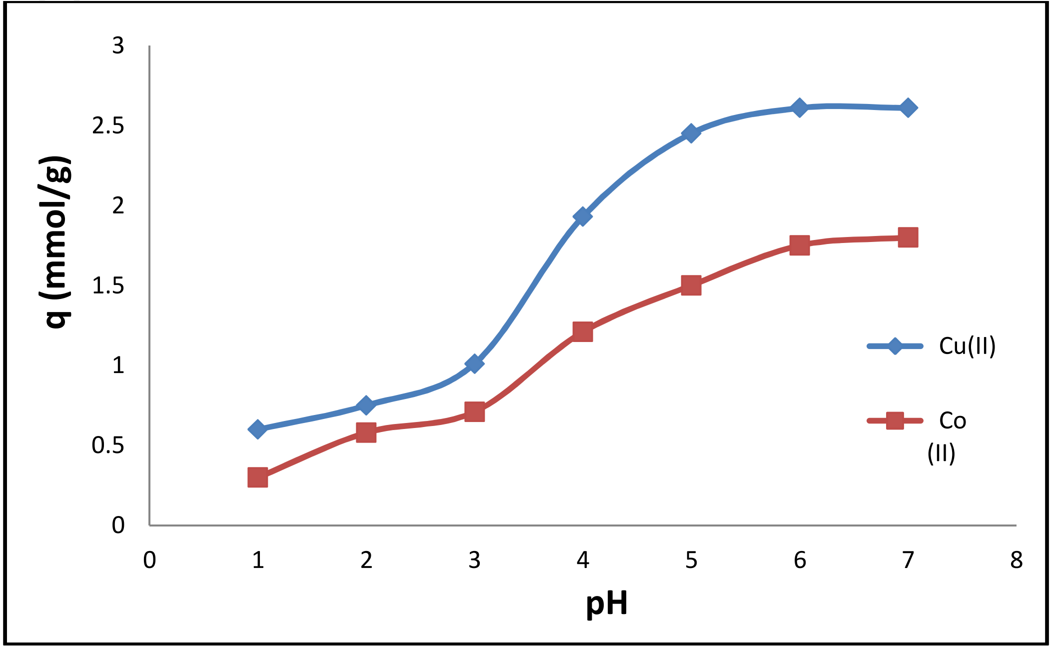


Figure 6. Effect of pH on the adsorption capacity of Cu (II) and Co (II)

Adsorption kinetics of biosorbent to Cu (II) and Co (II)

The influence of contact time on the adsorption capacity of CMC/KC/GO GBs at constant other adsorption conditions is shown in Fig7which reveal that the adsorption capacity of GBs towards metal ions increased rapidly in the first 3h,then slowed down and almost reach equilibrium at 210 min. therefore this optimum value is selected for the next adsorption process. The adsorption results were used to study the kinetic mechanism which controls the adsorption process. The most widely used models of Lagergren's pseudo-first-order, pseudo second - order, and intra particle diffusion were used to study the adsorption kinetics of Cu(II) and Co(II) on CMC/KC/GO GBs The pseudo first- order model is described in equation (2)while pseudo second- order is represented in equation (3)

$$\ln (q_e-q_t) = \ln q_e - K_1 t \qquad \textbf{(2)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q^2} + \left(\frac{1}{q}\right) t \qquad \textbf{(3)}$$

Where q_e(mmol/g) and q_t(mmol/g) are the adsorption capacity of CMC/KC/GO GBs at equilibrium and at a time t(h),respectively, K_1 and k_2 are the rate constants of the pseudo first-order and pseudo second-order models [28, 29].The intraparticle diffusion is proposed by Weber and Morris [30] was obtained by the next equation

$$q_t = K_{int}\, t^{0.5} \qquad \textbf{(4)}$$

Where K_{int} is the rate constant of the intra particle diffusion step mmol/g $min^{-0.5}$ The constant of the first-order, second-order and intra particle diffusion model were listed in Table 1.These results reveal that the order of correlation coefficient $R^2 \approx$ one is in the pseudo second- order model is > pseudo first -order model which indicate that the pseudo -second order model is a better model for describing the adsorption kinetics of Cu(II) and Co (II) on the GBs Furthermore , the calculated adsorption capacity values from the pseudo second order model are in a good agreements with the experimental values. when the plot q_t against $t^{0.5}$gives straight line ,this means that the intra particle diffusion represented as the only rate limiting step, but when the plot gives multi -

linearity indicates the step of the intra particle diffusion is one of several steps in the adsorption process[31]

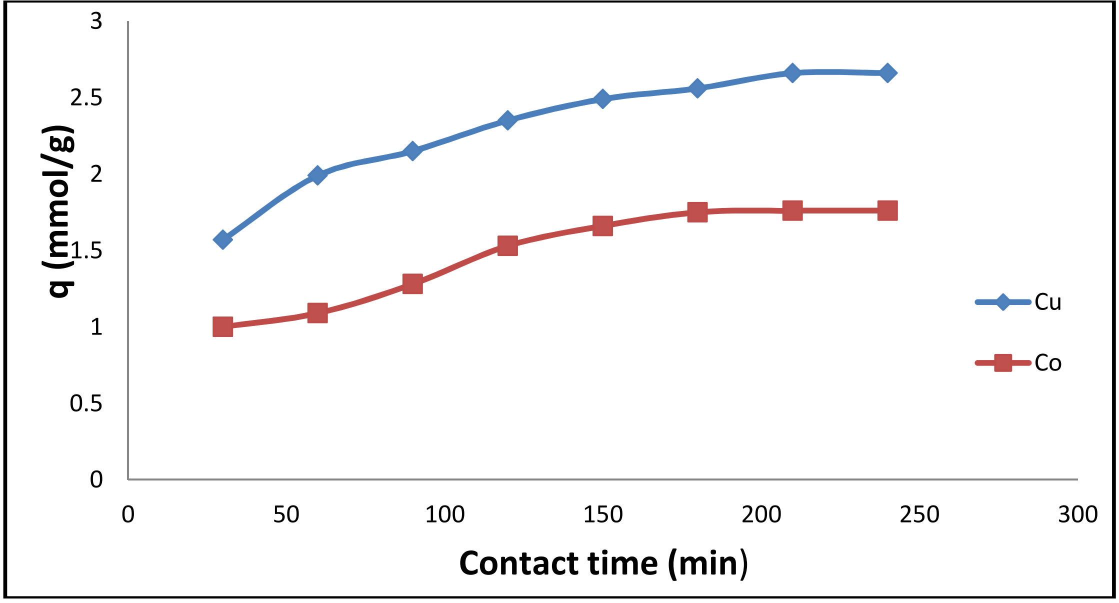


Figure 7. Effect of contact of contact time on the adsorption capacity of Cu (II) and Co (II)

Table 1: First-order, second- order and intra particle diffusion rate constants.

Metal ion	**Pseudo-first order kinetics**			**Pseudo-second-order kinetics**			**Intra particle diffusion**	
	q (mmol/g)	**K_{ads} (1/min)**	**R^2**	**Q mmol/g**	**K_2**	**R^2**	**K_{id}**	**R^2**
Cu(II)	**0.015**	**1.833**	**0.990**	**3.03**	**0.0104**	**0.997**	**0.116**	**0.976**
Co(II)	**0.016**	**1.518**	**0.927**	**2.079**	**0.01121**	**0.988**	**0.096**	**0.959**

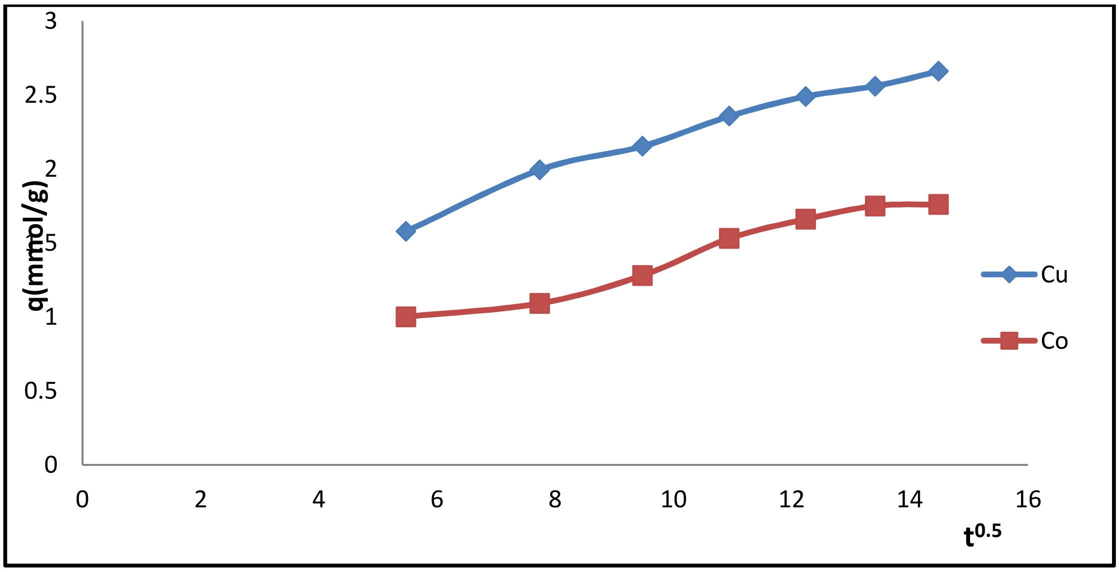


Figure 8. Plot of Weber-Morris intra particle diffusion model for the adsorption of Cu (II) and Co (II)

In figure 8 the adsorption process by the adsorbents occurs through three steps, which are transfers of metal ion from the bulk solution to the adsorbent surface, film diffusion in the pores and in the solid phase, and finally ion adsorption on the active sites of the adsorbents

Effect of the initial concentration of metal ions, and equilibrium isotherm model

The effect of initial concentration of Cu(II) and Co(II) ions was elaborated by shaking 0.5 g of GBs with 25 ml of metal ion solution in a concentration range from 1to 12 mmol /L at optimum pH and at 25 ^{0}C for 3h the results were presented in Fig(9) .It was cleared that as the initial concentration of the metal ions increase the adsorptive capacity increased and when the C_e value above 9mmol/L for Cu and 8.55 mmol/L for Co the q_e values almost remained constant it was also observed that Cu(II) was adsorbed more than Co(II) by GBs because of its smaller ionic radius which allows it to take place easily in the pores of chelating GBs

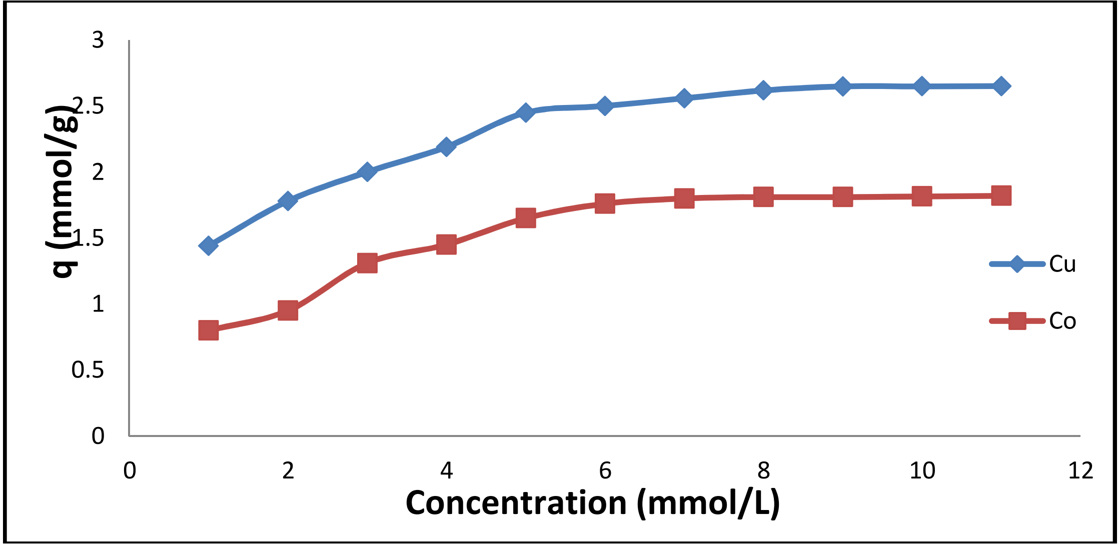


Figure 9. Effect of metal ions concentration on the adsorption capacity of Cu (II) and Co (II)

Two adsorption isotherm models were applied to describe the interaction between adsorbates and adsorbents Langmuir and Freundlich .The Langmuir isotherm model is represented in equation(5)

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{Kq_{max}} \qquad \mathbf{(5)}$$

Where C_e is the equilibrium concentration of metal ion mmol/L q_e is the equilibrium adsorption capacity mmol /g q_{max} is the maximum adsorption capacity and K (1/mmol) is the Langmuir constant concerned to the affinity of binding sites (32)

The dimensionless constant separation factor (R_L) (33) which reflect the essential characteristic of the Langmuir model, can be determined according to the next equation:

$$R_L = \frac{1}{1 + KC_0} \qquad \mathbf{(6)}$$

Where k is the Langmuir constant and C_o is the initial concentration of the metal ions (mmol/l). The value of R_L which is calculated recommends the shape of isotherm to be unfavorable ($R_L > 1$), favorable ($0 < R_L < 1$) or irreversible $R_L=0$. Plotting R_L versus C_o is illustrated in fig (10) .The calculated values of R_L were between zero and one for Cu and Co ions which detected that the adsorption of metal ions on the beads is favorable (34, 35)

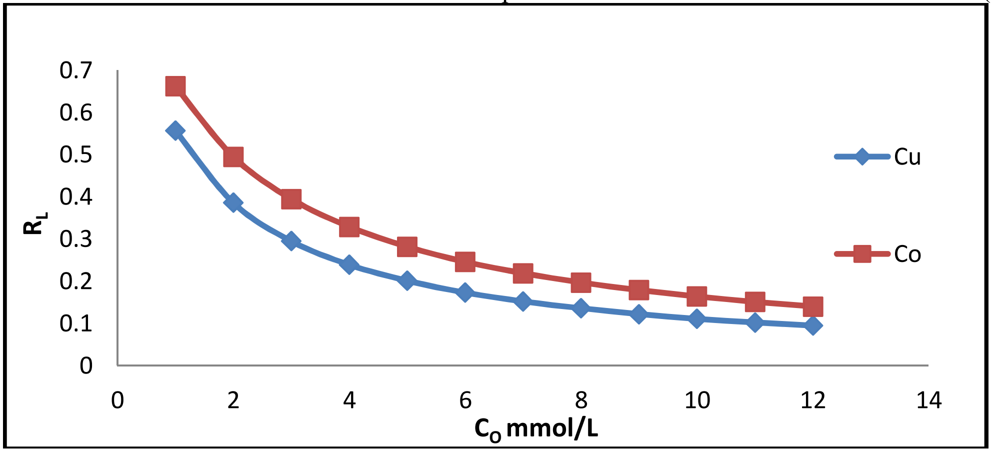


Figure 10. Variation of the adsorption intensity (R_L) with the initial metal ions concentration C_o

The Freundlich isotherm model is represented by the next equation [36]

$$\log q_e = N \log C_e + \log K_F \qquad \mathbf{(7)}$$

Where q_e is the equilibrium adsorption capacity (mmol/g)C_e is the equilibrium concentration of metal ions (mmol /L) K_F and N are the Freundlich constants that give information about heterogeneity degree of the surface sites. The characterization parameters of the Langmuir and Freundlich isotherm are listed in Table 2, it was shown from the table that the data of the adsorption of metal ions by GBs fit the Langmuir model nicely. The coefficient of determination $R^2$of the Langmuir isotherm is much nearer one than that of Freundlich isotherm model. Moreover, the calculated adsorption capacity from the Langmuir model is much closer the experimental value than that obtained from the Freundlich model also the value of N for Cu (II) and Co (II) between zero and one referred that the metal ion adsorption on the GBs was favorable [37].

Table 2: Parameters of Langmuir and Freundlich

Metal ion	**Langmuir isotherm**			**Freundlich isotherm**		
	Q_{max}	**K**	**R^2**	**N**	**K_f**	**R^2**
Cu(II)	**2.99**	**0.793**	**0.998**	**0.275**	**1.475**	**0.976**
Co(II)	**2.212**	**0.509**	**0.989**	**0.412**	**0.778**	**0.916**

Adsorption thermodynamic

The adsorption experiments were carried out at three different temperatures (30, 40, and 50) to calculate parameters of thermodynamic, in these experiments, metal ion solution (100 ml of 1mmol /L) with o.5 gm of GBs at optimum pH

Thermodynamic parameters were calculated using equation (8) and (9) (38)

$$\Delta G^0 = -RT \ln k_d \qquad \textbf{(8)}$$

$$\ln k_d = \frac{\Delta S^o_{ads}}{R} - \frac{\Delta H^o_{ads}}{RT} \qquad \textbf{(9)}$$

where k_d is the distribution coefficient ($k_d = q_e/c_e$),T is the temperature ,R is the gas constant (8.314 J/mol k) ΔG^o is the change of Gibbes free energy ΔH^o_{ads} the standard enthalpy change ΔS^o, is the standard entropy change ,both ΔH^o_{ads} and ΔS^o_{ads} were estimated by plotting $\ln k_d$ versus 1/T .The thermodynamic parameters are listed in Table3 ,the positive quantities of ΔH^o_{ads} refer that metal ion adsorption was an endothermic process [39] the negative value of ΔG^o indicate that the process was spontaneous and the increase of the negative value indicates that the adsorption process is more favorable at high temperature .The value of ΔS^o is positive ,suggesting the increase in the randomness of the system during the adsorption process which may be due to the release of water of hydration through the adsorption process[40].

Reusability

The regeneration of loaded GBs with Cu (II) and Co (II) was studied using 100 ml of 0.2 N HCl solutions at room temperature under shaking at 50 rpm for 1h. The recovered gel beads were filtered and washed with distilled water, the regenerated beads were used in the next adsorption cycle according to the same procedure to check the reusability of the beads, six successive adsorption- desorption cycles were conducted. The results referred that the gel beads were qualified for practical application as the adsorption capacity shows no significant change after six cycles of adsorption- desorption.

4. Conclusion

In this study new eco - friendly CMC/KC/GO GBs was prepared and characterized. The gel beads have a porous structure with an abundant adsorption active sites and a large contact surface because of the cross-linking and encapsulating of GO. Such special structure brought about a higher adsorption capacity for the GBs towards metal ions adsorption than that of the many adsorbents reported .The kinetic data described well by the pseudo-second order model and the Langmuir isotherm model is more favorable for adsorption isotherm of these metal ions. The thermodynamic parameters indicate that the process of adsorption is endothermic and spontaneous in nature. The GBs were regained by using0.2N HCl solution and could be used for six times. From the viewpoint of environment and economy, this biosorbent attract a great interest as a more environmental and cost-effective alternative, as this method of preparation is simple, economical and environmentally friendly.

References

1. Paulino, A.T., Minasse, F.A.S., Guilherme, M.R., Reis, A.V., Muniz, E. & Nozaki, J. (2006). Novel adsorbent based on silkworm chrysalides for removal of heavy metals from wastewater. J Colloid Interface Sci, 301:479-487.
2. Apostoli, P., Catalani, S., Zaghini, A., Mariotti, A., Poliani, P.L., Vielmi Semeraro .F, Duse, S., Porzionato, A., Macchi, V., Padovani, A., Rizzetti ,M.C.& De Caro ,R. (2012). High dose of Cobalt induce optic and auditory neuropathy. Exp Toxicol Pathol, 65 : 719-727
3. Wu, Y., Wang, Y., Wang, J., Xu , Yu, L., Philippe, C.& Wintgens, T. (2016) Nitrate removal from water by new polymeric adsorbent modified with amino and quaternary ammonium groups :batch and column adsorption study .J Taiwan Inst Chem , E66: 191–199.
4. Ngomsik, A.F., Bee, A., Siaugue, J.M., Cabuil, V. & Cote, G. (2006) Nickel adsorption by magnetic alginate microcapsules containing an extractant. Water Res, 40 (9):1848–1856.
5. Guibal, E., Vooren, M.V., Dempsey, B.A. & Roussy, J. (2006) A review of the use of chitosan for the removal of particulate and dissolved contaminants. Sci. Technol, 41(11): 2487–2514.
6. Wang, N., Jin ,R.N., Omer, A.M.& Ouyang, X.K. (2017) Adsorption of Pb(II) from fish sauce using carboxylated cellulose nanocrystal: isotherm, kinetics, and thermodynamic studies. Int J Biol Macro mol, 102 : 232–240.

7. O'Connor, S.M.O& Gehrke, S.H. (1997) Synthesis and characterization of thermally-responsive hydroxypropyl methylcellulose gel beads. J Appl Polym Sci 66 (7): 1279–1290.
8. Li, N. & Renbi, B. (2005) A novel amine-Shielded surface cross-Linking of chitosan hydrogel beads for enhanced metal adsorption performance. Ind. Eng. Chem,44 (17) : 6692–6700.
9. Gorgieva , S.& Kokol,V.(2011) Synthesis and application of new temperature-responsive hydrogels based on carboxymethyl and hydroxyethylcellulose derivatives for the functional finishing of cotton knitwear. Carbohydr. Polym, 85(3): 664–673.
10. Bao, Y., Ma, J. & Li, N. (2011) Synthesis and swelling behaviors of sodium carboxymethylcellulose-g-poly(AA-co-AM-cAMPS)/superabsorbent hydrogel Carbohydr Polym ,84(1) :76–82.
11. Pourjavadi, A., Barzegar, S.& Mahdavinia, G.R. (2006) MBA-crosslinked Na-Alg /CMC as a smart full-polysaccharide superabsorbent hydrogels, Carbohydr. Polym, 66(3): 386–395.
12. Meena, R., Prasad, K.& Siddhanta, A.K. (2009) Development of a stable hydrogel network based on agar–kappa-carrageenan blend cross-linked with genipin. Food Hydrocoll,23:497–509.
13. Duman, O., Tunc, S., Plot, T.G.& Bozog˘lan, B.K.(2016) Synthesis of magnetic oxidized multiwalled carbon nanotube-j-carrageenan-Fe3O4 nano composite adsorbent and its application in cationic Methylene Blue dye adsorption. Carbohydr polym, 147:79-88
14. Zhang, Z., Zhang, R., Chen, L.& Mc Clements, D.G.(2016) Encapsulation of lactase(b-galactosid)into k-carrageenan-based hydrogel beads:Impact of, environmental conditions on enzyme activity. Food Chem, 200:69–75.
15. Mahdavinia, G.R.,Aghaie, H., Sheykhloie, H., Vardini, M.T.& Etemadi H(2013) Synthesis of Car Alg /MMt nano composite hydrogels and adsorption of cationic crystal violet . Carbohydr.Polym, 98:358–365.
16. Ramesha, G.K., VijayaKumara, A., Muralidhara, H.B.& Sampath, S.(2011) Graphene and grapheneoxide as effective adsorbents toward anionic and cationic dyes.J.Colloid Interface Sci,361 :270–277.
17. Yang, S.T., Chen, S., Chang, Y., Cao, A. , Liu ,Y.& Wang, H. (2011) Removal of methylene blue from aqueous solution by graphene oxide. J Colloide Interface Sci 359:24-29.
18. Gan, L., Li, H., Chen, L.W., Xu ,L., Liu, J., Geng ,A., Mei ,C.& Shang ,S. (2018) Graphene oxide incorporated alginate hygrogel beads for the removal of various organic dyes and bisphenol A in water. J Colloide and polymer sci, 296: 607-615
19. Moharram, M.A.K., Tohami, K., El Hotoby ,W.M.& Bakar, A.M. (2016) graphene oxide porous crosslinked cellulose nanocomposite microsphere for lead removal: kinetic study. J Reactive and functional polymer, 101:9-19
20. Yang, M., Liu, X., Qi, Y., Sun, W. & Men, Y. (2017) preparation of carrageenan/graphene oxide gel beads and their efficient adsorption for methylene blue. J Colloide Interface science, 506:669-677
21. Hummers, W.S., Offeman, R.E. (1958) Preparation of graphitie oxide. J Am Chem Soc, 80:1339-1347
22. Qi, Y., Yang, M., XU, W., He, S. & Men, Y. (2017) Natural polysaccharides- modified graphene oxide for adsorption of organic dyes from aqueous solutions. J Colloide interface Sci, 486:84-96
23. Liu, K., Zhang, J., Yang, G., Wang, C.& Zhu, J.(2010) Direct elctrochemistry , and electro catalysis of hemoglobin-based on poly (diallyl dimethylammonium chloride)functionalized graphene sheets/room temperature ionic liquid composite film . Electrochem Commun,12:402-405
24. Zhang, D-D., Zu S-Z&Han B-H(2009) Carbon 47:2993-3000
25. Fan, L., Luo, C., Sun, M., Qiu, H.& Li, X.(2013) Synthesis of magnetic b-cyclodextrin–chitosan/grapheneoxide as nano-adsorbent and its application in dye adsorption and removal.Colloids Surf. B Biointerfaces, 103:601–607.
26. Chio, Liu, Omer, A.M. & Xiao-Kun, Q. (2018) Adsorptive removal of cationic methylene blue dye using carboxymethyl cellulose /k-carrageenan activated montmorillonite composite beads: isotherm and kinetic studies. Int J Bio Macromol, 106:823-833
27. Yakout, A.A., El-Sokkary, R.H., Shreadah, M.A.& Omnia, G . (2017) Cross-linked graphene oxide sheets via modified extracted cellulose with metal adsorption. Carbohydrate Polymers, 172:20-27
28. Han, X., Wang, W.& Ma , X. (2011) Adsorption characteristics of methylene blue onto low cost biomass material lotus leaf.Chem Eng.J,171:1–8.
29. Song, W., Gao, B., Xu, X., Xing, L., Han, S., Duan, P., Song, W.& Jia, R.(2016) desorption behavior of magnetic amine/Fe3O4functionalized biopolymer resin towards anionic dyes from wastewater.Bioresour.Technol,210 (2016) 123–130
30. Weber, W.J. & Morris, J.C. (1964) Equilibrium and capacities for adsorption on carbon. J Sanitary Eng Div, 90:79-91.
31. Sarici –Ozdemir C. & Onal ,Y. (2010) Equilibrium, kinetic and thermodynamic adsorption of the environmental pollutant tannic acid onto activated carbon. Desalination, 251: 146-152
32. Langmuir, L. (1918) the adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc, 40:1361-1403

33. Weber, T.W. & Chakravot, R. K. (1974) Pore and solid diffusion models for fixed bed adsorbents. AlChE J, 20:228-238
34. Sari, A., Tuzen, M., Citak, D. & Soylak, M.(2007) Equilibrium, kinetic and thermodynamic studies of adsorption of Pb (II) from aqueous solution onto Turkish kaolinite clay .J Hazard Mater, 149:283-291
35. Wang, X.S., Huang, J., Hua, H.Q, Wang, J. & Qin, Y.(2007) Determination of kinetic and equilibrium parameters of the batch adsorption of Ni(II) from aqueous solutions by Na-mordent. J Hazard Mater, 142:468-476
36. Freundlish, H.(1906) Adsorption in solution .Phys Chem Soc, 40:1361-1368
37. Shappan A.F., Khalil A.A., Mohammed Radwan, Manal El Hefnawy, El Kawaga H.A.(2017) Synthesis, characterization and application of a novel nanometer- sized chelating resin for removal of Cu(II),Co(II) and Ni(II) from aqueous solutions. J Polym Res ,2 4:165-171
38. Ai, L., Zhang,C.&Chen,Z.(2011)Removal of methylene blue from aqueous solution by solvothermal-synthesized graphene/magnetite composite. J. Hazard Mater, 192:1515-1524
39. Özcan, A.S. & Özcan A.(2004) Adsorption of acid dyes from aqueous solutions onto acid activated bentonite. J Colloid Interface Sci, 276:39–46
40. Namasivayam,C.,Yamuna,R.T.(1995) Adsorption of directed 12B by biogas residual slurry: Equilibrium and rate processes. Environ pollut, 89:1-9