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Enhanced removal of Chloramphenicol drug by low cost superabsorbent hydrogel nanocomposite: Optimization, isotherm, and thermodynamic modelling non-linear

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ABSTRACT
In this work, an eco-friendly, stable, simple, new super adsorbent adsorption properties based on biopolymer sodium alginate was successfully deliberated by a combination of a simple crosslinking method. We prepared two hydrogel including (SA-g-P(Ac-co-AM) hydrogel and the second hydrogel after loading CNT/ZnO onto hydrogel. These new hydrogel surfaces were prepared from two monomers (acryl acid and acrylamide) to remove Chloramphenicol CHZ drug. The physical characterizations of new super adsorbent hydrogel nanocomposite were evaluated by XRD, FTIR, TGA, EDX and TEM. The practical experiments involved calculation of the best wavelength and study of best condition of adsorption factors such as effect of equilibrium time, weight of hydrogel nanocomposite, temperature solution, pH solution, and adsorbent regeneration experiments (Desorption). The removal percentage of CHZ drug increased from 55.45 to 89.8%, and adsorption capacity was changed from 65.5 to 110 mg g^{-1} on to hydrogel nanocomposite. The isotherm Freundlich and isotherm Langmuir were too introduced. All data followed the model Freundlich isotherm in the presence of CHZ drug. The change enthalpy (ΔH) value was positive indicating the adsorption method endo-thermic presses and spontaneous of change Gibes free energy (ΔG) negative value, as well as positive value of change entropy (ΔS).

Keyword: Hydrogel, Nanocomposite, Drug, Chloramphenicol, Isotherm, Thermodynamic.
Article type: Research Article.

INTRODUCTION
Due to the significant increase in pollution problems in recent decades, scientists around the world, especially in industrialized and developed countries, have tended to pay attention to this problem and to establish international committees for environmental protection. They focused on developing protocols that reduce or treat pollution during or after manufacturing. In medicine, significant concentrations of drug compounds and raw materials for drug manufacturing can be found in large amounts of hospital waste and pharmaceutical factories. One of the most effective techniques that meets the recommendations of the international committee is adsorption, which is considered the most efficient technique used in the separation and purification processes (Aljeboree *et al.* 2019). The recent literature survey of the waste treatment and green chemistry methodologies exhibited that the adsorption technique was highly used for removing pharmaceutical chemicals and industrial dyes in various waste water (Aljeboree & Alkaim 2019; Alkaim & Ajobree 2020). Chloramphenicol chemically D-threo-(1R,2R)-1-p-Nitrophenyl-2-dichloroacetamido-1,3-propanediol is a semi-synthetic antibiotic that belongs to the class of nitrobenzene derivative drugs with a wide spectrum of activity toward both gram-negative and gram-positive bacteria (Mahmoud 2007). It is most commonly used to treat bacterial conjunctivitis, an infection of the mucous membrane of the eyes (Mahmoud 2007). Due to its good pharmacokinetic features, high penetration into the tissues, and low manufacturing cost, it is used as the drug of choice to treat numerous infectious diseases in food-

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producing animals (such as honeybees). Chloramphenicol has several impurities and related compounds that may coexist with the active substance in the pharmaceutical dosage form of the drug. These impurities can increase the side effects of a drug and change its activity (Aljeboree & Alshirifi 2019). Chloramphenicol and related compounds have been linked to a number of adverse effects in humans, including leukaemia, gastrointestinal disorders, fatal aplastic anaemia, bone marrow depression, and allergic reactions (Tassew Alemayehu 2013; Aljeboree & Alshirifi 2018).

MATERIALS AND METHODS

Preparation of nanocomposite hydrogel

The free radical polymerization of nanocomposite based on crosslinking N, N'-Methylene bis-acrylamide MBA was prepared. Then 0.2 g ZnO/CNT was taken in 20 mL distilled water. At room temperature, sodium alginate (SA) 5% was prepared and added to the ZnO/CNT mixture followed by adding 0.5 g acrylamide AM and 3 mL acrylic acid (AC). Afterward, 0.05 g potassium persulfate (KPS, as a free radical initiator for polymerization) was added with 0.05 g N, N'-Methylene bisacrylamide (MBA, as an acrylamide cross-linking agent). Then, the reaction mixture was heated at 75 °C in a water bath.

Adsorption Isotherm

The batch adsorption method was used to investigate the adsorption behaviour of two drug onto super non-absorbent hydrogel (SA-g-P(Ac-co-AM)/ZnO-CNT). A known quantity of hydrogel (0.1g) in a 100-mL solution containing 100 mg L^{-1} quantity of two drug derivatives in 100-mL Erlenmeyer flasks. The reaction mixture was placed in shaker water bath for 60 min and then centrifuged for 10 min. The remaining pollutant concentrations in the resultant supernatant were determined using the proposed method. The adsorption capacity (Qe) and percentage (E%) adsorption was estimated in Eqs. 1-2.

$$\mathrm{Qe}\left(\frac{\mathrm{mg}}{\mathrm{g}}\right)=\frac{(\mathrm{Co}-\mathrm{Ce})\mathrm{Vml}}{\mathrm{M\ gm}} \qquad (1)$$

$$\mathrm{E}=\frac{\mathrm{Co}-\mathrm{Ce}}{\mathrm{Co}}\times 100 \qquad (2)$$

RESULTS AND DISCUSSION

Characterization of hydrogel nanocomposite

FTIR technique was utilized to analyse the surface functional groups responsible for CHZ adsorption. Adsorbent surfaces hydrogel nanocomposite and drug-loaded surface after adsorption were placed in an oven at 70 ℃ for 24 h. The FTIR spectra exhibited the hydrogel nanocomposite before and after adsorption. The broadband around 3525 cm^{-1} and 1600 cm^{-1} were characteristics of the stretching of the –OH groups and the C=O, respectively. Also teeth like peaks in the region around 400-650 cm^{-1} of Zn-O bending were observed which confirmed the impregnation of ZnO nanoparticles (Fig. 1).

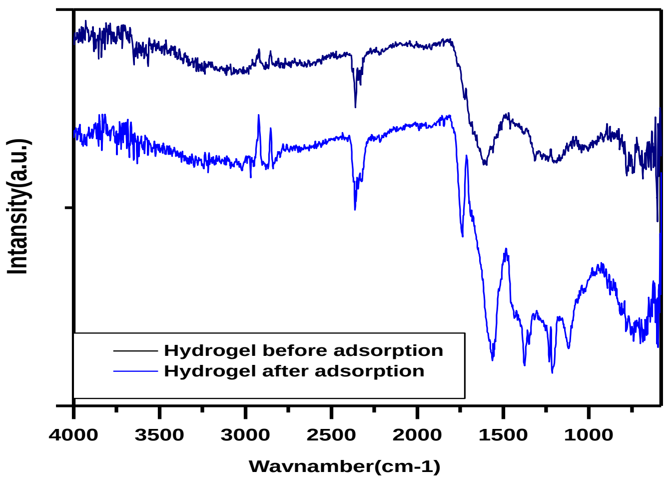

Fig. 1. FTIR spectra characterize of hydrogel nanocomposite.

The TGA Analysis of SA-g-P(Ac-co-AM)/ZnO-CNT hydrogel nanocomposite, shown in Fig. 2 gives added confirmation that ZnO/CNT integrates into hydrogel (Zhou *et al.* 2013). A loss weight at range temperature of 5-650 °C, of which 11.322% was happened at temperatures less than 200 °C evaporation of the free water and 42.13% in the range temperature of 200-400 °C due to desorption water and volatility (Luo 2020; Yasin *et al.* 2021).

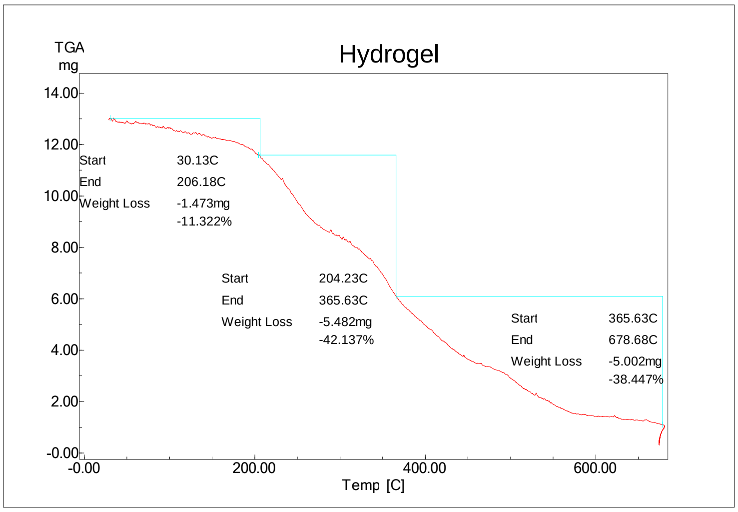

Fig. 2. TGA Analysis of hydrogel nanocomposite.

The crystalline of SA-g-P(Ac-co-AM)/ZnO-CNT hydrogel nanocomposite was analysed via X-ray diffraction and the registered patterns (Fig. 3). SA-g-P(Ac-co-AM)/ZnO-CNT) hydrogel nanocomposite X-ray diffraction type refers to the semi-crystalline of the nanocomposite with one broad peak at 2θ° = 20 .32 related indicate the dispersion of CNT into the polymeric network. In addition, the appearance of crystalline peaks in 2θ° = 32 .32, 2θ° = 34 .32 and 2θ° = 36 .33 indicate the loading of zinc oxide nanoparticles.

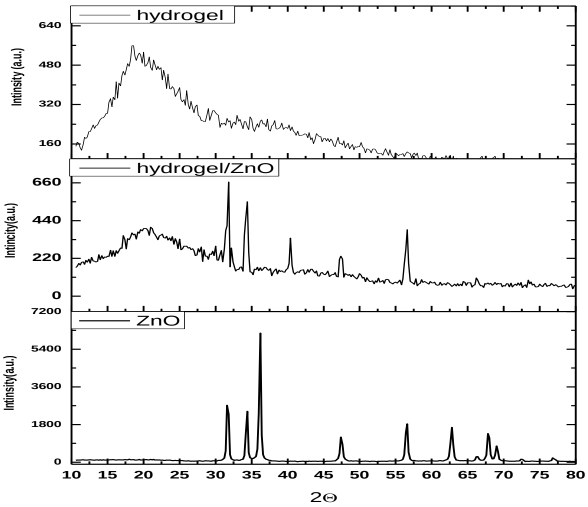

Fig. 3. X-ray diffraction: a) ZnO NPs; b) hydrogel; c) hydrogel nanocomposite.

Transmittance Electron Microscopy (TEM) and Energy Dispersion X-ray (EDX; Fig. 4a) show image of TEM ZnO; Fig. 4b exhibits CNT where ZnO/CNT was observed embedded inside the hydrogel nanocomposite (Fig. 4c). In addition, incorporation of CNT/ZnO into hydrogel is supported via the presence of Zn and O, C peak in the EDX of hydrogel nanocomposite (Fig. 4f). The synthesized nano-composite have elements O, C, and Zn. Values of the lowest and highest elements existing in the modified hydrogel nanocomposite are 15.9 wt.% and 75.7 wt.%, respectively.

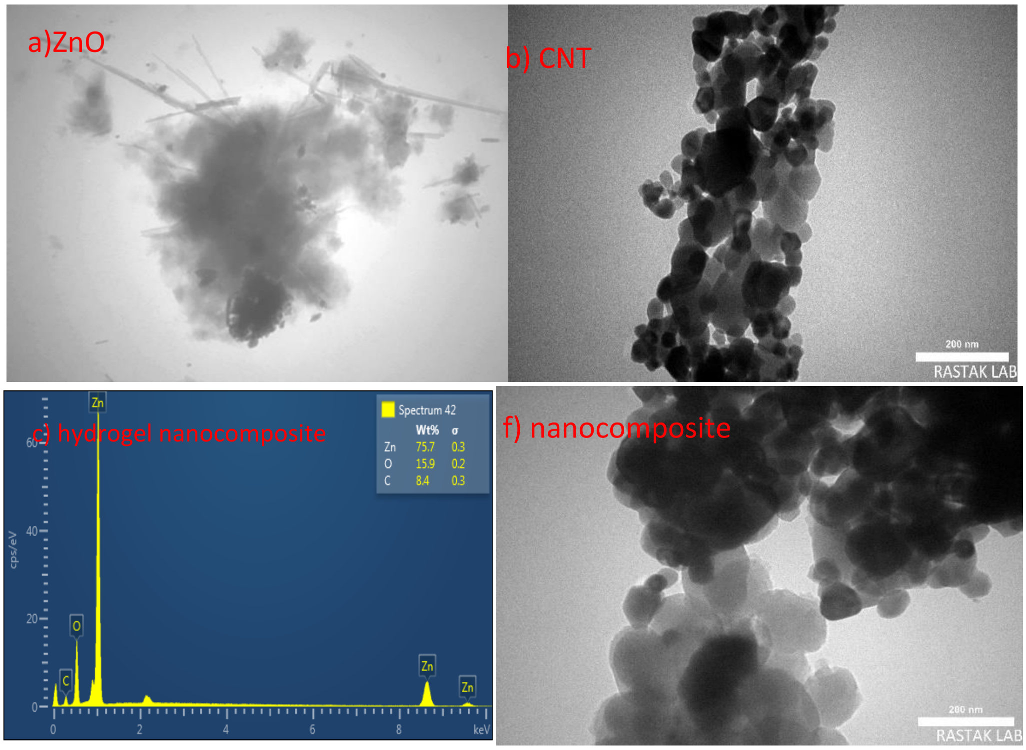

Fig. 4. TEM; a) ZnO NPs; b) CNT; c) hydrogel nanocomposite and EDX; f) hydrogel nanocomposite.

Effect of different parameter

Effect of equilibrium time

Equilibrium time is very significant parameter moving the capacity of adsorption. To study the elimination of CHZ drug utilizing absorbance hydrogel nanocomposite analysis is carried out utilizing the previously estimated best solution pH 7, weight of nanocomposite (0.1 g) and concentration of drug (100 mg L^{-1}; Zheng *et al.* 2020). In this batch study samples were taken at several interval ranging from 2 to 120 min. The best adsorption occured within 1h. The best value of contact time was 1 h after which the adsorption becomes constant (Fig. 5; Esmaeili *et al*. 2021; León *et al.* 2021).

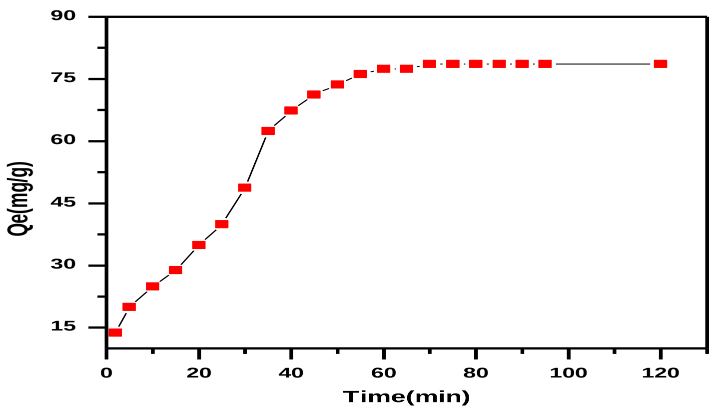

Fig. 5. Effect of equilibrium time of CHZ drug onto hydrogel nanocomposite.

Effect of pH

The effect of solution pH on the adsorption of CHZ drug onto hydrogel nanocomposite was studied at range solution pH of 2-10 in the presence of concentrations of CHZ drug (100 mg L^{-1}; Fig. 6). The equilibrium sorption efficiency of CHZ drug onto hydrogel nanocomposite was very little in pH 2, the adsorption efficiency of solution in pH 2 of hydrogel nanocomposite l (91.106 mg g^{-1}). When the solution pH is larger than 6 the sorption efficiency of CHZ drug onto hydrogel nanocomposite increases by elevating values of pH.

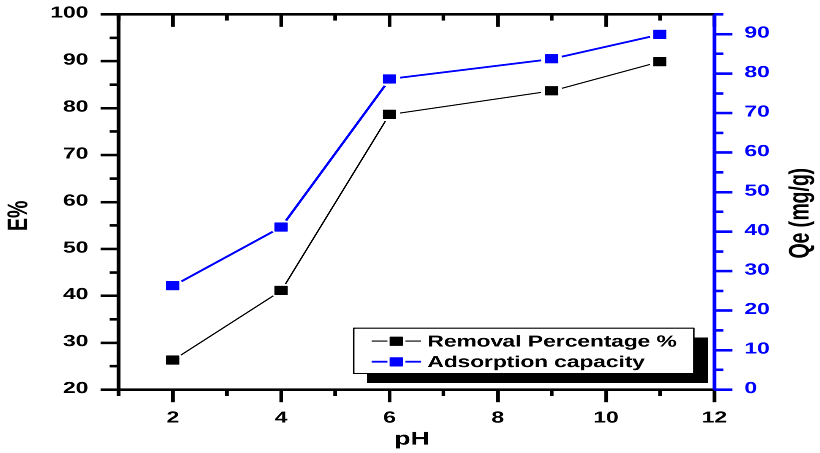

Fig. 6. Effect of solution pH of CHZ drug onto hydrogel nanocomposite.

Effect of weight of nanocomposite

The effect of the weight of nanocomposite was necessary to observe the least possible quantity, which shows the maximum adsorption stoichiometric. The quantities of the adsorbent were varied from 0.05 to 0.13 g/100 mL of hydrogel nanocomposite (Fig. 7). An increase in the percentage of CHZ drug removal by adsorbent mass was related to elevations in the adsorbent surface areas, enhancing the number of adsorption sites available for adsorption as reported already in other cases. The increase in removal of CHZ drug by adsorbent dose is due to the introduction of more binding sites for adsorption (Yasin *et al.* 2021; Aljeboree *et al.* 2021). The primary factor explaining this characteristic is that adsorption sites remain unsaturated during the adsorption reaction, whereas the number of sites available for adsorption site increases by upraising the adsorbent dose (Luo *et al.* 2022; Al Niaeem & Hanoosh 2022).

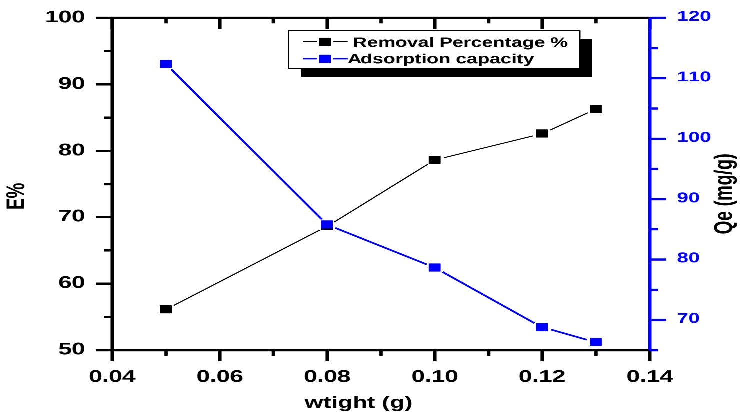

Fig. 7. Effect of weight of hydrogel nanocomposite

Effect of temperature

To determine whether the ongoing adsorption method was endo-thermic or exo-thermic, the adsorption isotherms were limited for several drug-adsorbent methods. The percentage removal of drug was examined at several solution temperatures (15-35 ºC) in the presence of different primary concentrations of CHZ (10-100 mg L^{-1}) and data are shows in Fig. 8. The data exhibited that the equilibrium adsorption efficiency of CHZ drug was increased by rising in temperature of solution for wholly primary CHZ drug concentrations. The uptake ability of hydrogel nanocomposite raised by elevating in solution temperature, due to the improve quantity of the reverse step (desorption) in the mechanism. This is probably due to the endo-thermic effect of the surroundings through the adsorption method (Alshamri *et al.* 2021).

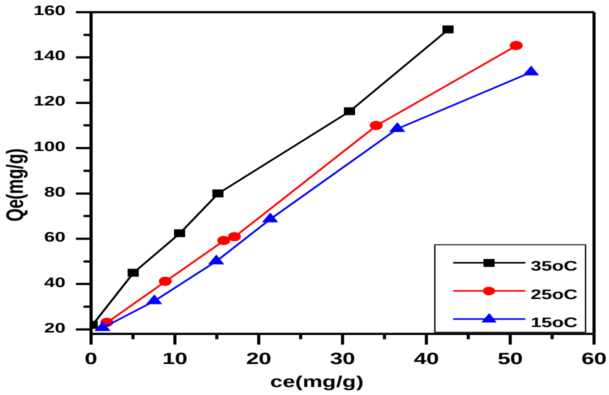

Fig. 8. Effect of solution temperature on the adsorption of CHZ drug onto hydrogel nanocomposite.

The thermodynamic study useful in this work were change free energy (ΔG), change enthalpy (ΔH), and change entropy (ΔS). Van't Hoff equation was utilized to estimate the thermos-dynamic factors as following in equations 3-5.

$$K_e = \frac{(Q_{max}) * Wt\ (0.1\ gm)}{(C_e) * V(0.1L)} \times 1000 \qquad (3)$$

$$\Delta G = -RT \ln K_e \qquad (4)$$

$$\ln X_m = -\frac{\Delta H}{RT} + Cons. \qquad (5)$$

The quantitative thermos-dynamic result of CHZ drug on the adsorbent hydrogel nanocomposite is presented in Table 1. This Table depicts the values of ΔH for CHZ drug which is positive indicating that the adsorption method is endo-thermic. All methods of adsorption were considered spontaneous from the ΔG negative value, while positive value of ΔS for CHZ drug (Abdalghaffar & Tawfik 2020).

Table 1. Thermodynamic parameter ΔS ΔG and, ΔH for CHZ drug adsorbed onto hydrogel nanocomposite.

Thermodynamic Factors			
ΔH(kJ/mol)	**ΔG(kJ/mol)**	**ΔS(kJ/Kmol)**	**Equilibrium Constant(Ke)**
8.8211	-3.311	70.144	3.36

Adsorption isotherm

To give details the adsorption capacity of the hydrogel nanocomposite, the equilibrium investigational data were studied to confirm compliance with the equations model of Langmuir isotherm and Freundlich isotherm (Powers 2003; Gamoudi & Srasra 2019). Freundlich Isotherm is an experiential equation based on adsorption onto heterogeneous surface, as calculating in Eq. 6

$$Q_e = k_f\, C_e^{\frac{1}{n}} \qquad (6)$$

Langmuir Isotherm is used for the adsorption of a solute from solution as adsorption monolayer on a surface taking number finite of identical sites (del Mar Orta *et al.* 2019). The model is setup on different essential assumptions: (i) the sorption occurs at set sites homogeneous adsorbent; (ii) once a dye molecule of site occupies; (iii) the adsorbent (at equilibrium) has ability limited for the adsorbate; (iv) total of sites are congruous and energetically identical. The non-linear equation of isotherm Langmuir is shown in eq. 7.

$$Q_e = \frac{Q_m\, K_L\, C_e}{1 + K_L\, C_e} \qquad (7)$$

The KF values and (R^2) found from Freundlich models as appear in Table 2. The adsorption of dye better fitted to Freundlich isotherm with the best R^2 = 0.9877 in comparison with Langmuir isotherm (Chayid & Ahmed 2015; Aljeboree & Alkaim 2019). The Freundlich isotherm has exhibited a better fitted to the adsorption data than the Langmuir isotherm (Fig. 9).

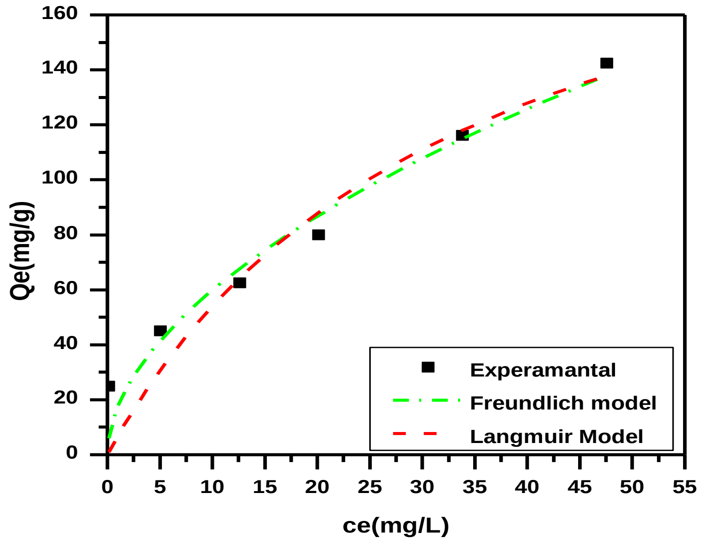

Fig. 9. Adsorption isotherm two model Freundlich and Langmuir Isotherm nanocomposite.

Table 2. several factor isotherm for the adsorption study of CHZ drug on to hydrogel nanocomposite

Hydrogel nanocomposite			
Freundlich	K_f	17.402	5.231±
	1/n	0.566	±0.084
	R^2	0.93899	
Langmuir	q_m (mg/g)	235.737	74.76±
	K_L (L/mg)	0.02	0.011±
	R^2	0.8891	

Reactivation of hydrogel nanocomposite

The re-use of nanocomposite, after sorption, is one of the important economic parameter for the treatment method. It helps in elucidating the mechanism of CHZ drug removal from drug -loaded adsorbent, reactivation mechanism and re-cycling of spent adsorbents, which in turn may reduce operational cost and protect the environment from secondary drug. The CHZ drug de-sorption studies were carried out using 0.01 N HCl. The performance and re-use of hydrogel nanocomposite via utilizing HCl in the CHZ drug adsorption method were studied up to steps 4 under best conditions (Fig. 10). After the 3 cycles of utilizing nanocomposite, the efficiency is still significant (>70%) and this shows that nanocomposite is possible renewable adsorber (Al Bayati 2020; Pashaei Fakhri *et al.* 2021).

CONCLUSION

The removal percentage E% and adsorption capacity of CHZ drug elimination raise by increasing surface area, equilibrium time, and solution temperature. However, decreasing the adsorption efficiency occurs by the elevated weight of hydrogel. The best equilibrium time for equilibrium reaction is 60 min. For CHZ drug on surfaces hydrogel nanocomposite, best adsorption was found at pH 10. Removal percentage raises by an elevation in solution pH.

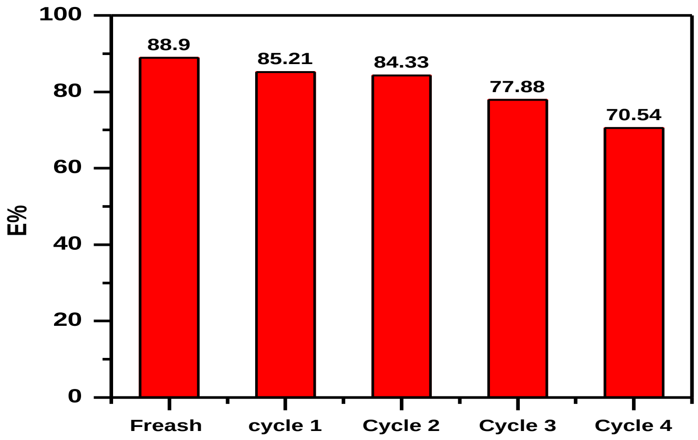

Fig. 10. Multi-cycle use of hydrogel nanocomposite

REFERENCES

Abdalghaffar, OAHM & Tawfik, AS 2020, Simultaneous adsorption of dye and toxic metal ions using an interfacially polymerized silica/polyamide nanocomposite: Kinetic and thermodynamic studies. *Journal of Molecular Liquids*, 314: 113640.

Al Bayati, RA 2020, Adsorption-desorption isotherm of one of antidiabetic drug from aqueous solutions on some pharmaceutical adsorbents. *European Journal of Scientific Research*, 40: 580-588.

Al Niaeem, HS & Hanoosh, W 2022, Preparation of semi IPNs-hydrogel composite for removing Congo Red and Bismarck Brown Y from wastewater: Kinetic and thermodynamic study. *Egyptian Journal of Chemistry*, 56: 19 - 34.

Aljeboree, AM & Alkaim, AF 2019, Comparative removal of three textile dyes from aqueous solutions by adsorption: As a model (corn-cob source waste) of plants role in environmental enhancement. *Plant Archives*, 19: 1613-1620.

Aljeboree, AM & Alkaim, AF 2019, Role of plant wastes as an ecofriendly for pollutants (Crystal Violet dye) removal from aqueous solutions. *Plant Archives*, 19: 902-905.

Aljeboree, AM & Alshirifi, AN 2018, Spectrophotometric determination of phenylephrine hydrochloride drug in the existence of 4-aminoantipyrine: Statistical study. *International Journal of Pharmaceutical Research*, 10: 576-584.

Aljeboree, AM & Alshirifi, AN 2019, Oxidative coupling of Amoxicillin using 4-Aminoantipyrine: Stability and higher sensitivity. In: *Journal of Physics*: Conference Series.

Aljeboree, AM, Al Baitai, AY, Abdalhadi, SM & Alkaim, AF 2021, Investigation study of removing methyl violet dye from aqueous solutions using corn-cob as a source of activated carbon. *Egyptian Journal of Chemistry*, 64: 2873-2878.

Aljeboree, AM, Hussein, FH & Alkaim AF 2019, Removal of textile dye (methylene blue MB) from aqueous solution by activated carbon as a model (corn-cob source waste of plant): As a model of environmental enhancement. *Plant Archives*, 19: 906-909.

Alkaim, AF & Aljeobree, AM 2020, White marble as an alternative surface for removal of toxic dyes (Methylene blue) from Aqueous solutions. *International Journal of Advanced Science and Technology*, 29: 5470-5479.

Alshamri, AM, Alqaragully, MB & Alkaim, AF 2021, Removal of toxic textile dyes from aqueous solution through adsorption onto coconut husk waste: Thermodynamic and isotherm studies. *Caspian Journal of Environmental Sciences*, 19: 513~522

Bashir, WA & Hamoudi, TA 2013, Spectrophotometric Determination of chloramphenicol in pharmaceutical preparations. *Journal of Education and Science*, 27: 19-35.

Chayid, MA & Ahmed, MJ 2015, Amoxicillin adsorption on microwave prepared activated carbon from Arundo donax Linn: Isotherms, kinetics, and thermodynamics studies. *Journal of Environmental Chemical Engineering*, 3: 1592-1601.

del Mar Orta, M, Martn, J, Medina Carrasco, S, Santos, JL, Aparicio, I & Alonso, E 2019, Adsorption of propranolol onto montmorillonite: Kinetic, isotherm and pH studies. *Applied Clay Science*, 173: 107-114.

Esmaeili, H, Foroutan, R, Jafari, D & Rezaei, MA 2021, Effect of interfering ions on phosphate removal from aqueous media using magnesium oxide@ferric molybdate nanocomposite. *Korean Journal of Chemical Engineering* ,37: 804-814.

Gamoudi, S & Srasra, E 2019, Adsorption of organic dyes by HDPy+-modified clay: effect of molecular structure on the adsorption. *Journal of Molecular Structure*.

León, G, Saura, F, Hidalgo, AM & Miguel, B 2021, Activated olive stones as a low-cost and environmentally friendly adsorbent for removing cephalosporin c from aqueous solutions. *International Journal of Environmental Research and Public Health*, 18: 4489.

Luo, Q, Ren, T, Lei, Z, Huang, Y, Huang, Y, Xu, D, Wan, C, Guo, X & Yiqiang, W 2022, Non-toxic chitosan-based hydrogel with strong adsorption and sensitive detection abilities for tetracycline. *Chemical Engineering Journal*, 427: 131738.

Luo, S 2020, ZnO nanorod arrays assembled on activated carbon fibres for photocatalytic degradation: Characteristics and synergistic effects. *Chemosphere*, 261: 127731.

Mahmoud, KM 2007, Determination of Chloramphenicol from pure and pharmaceutical preparations using FIAS pectrophotometric methods. *National Journal of Chemistry*, 28: 634-641.

Mohammed A Jawad, AJK & Radia, ND 2021, Role of sodium alginate-g-poly (acrylic acid-fumaric acid) hydrogel for removal of pharmaceutical paracetamol from aqueous solutions by Adsorption *International Journal of Pharmaceutical Quality Assurance*, 12: 202-205.

Pashaei Fakhri, S, Peighambardoust, SJ, Foroutan , R, Arsalani, N & Ramavandi, R 2021, Crystal violet dye sorption over acrylamide/graphene oxide bonded sodium alginate nanocomposite hydrogel. *Chemosphere*, 270: 129419.

Powers, HJ 2003, Riboflavin (vitamin B_2) and health. *The American Journal of Clinical Nutrition*, 77: 1352-1360.

Tassew Alemayehu, AS 2013, Determination of chloramphenicol in pharmaceutical samples at electrochemically pretreated glassy carbon electrode. *American Scientific Research Journal for Engineering, Technology, and Sciences* (ASRJETS), 6: 1-11.

Yasin, AS, Kim, DH & Lee, K 2021, One-pot synthesis of activated carbon decorated with ZnO nanoparticles for capacitive deionization application. *Journal of Alloys and Compounds,* 870: p. 159422.

Zheng, MC, Chen, M, Zhu, Y, Zhang, L & Zheng, B 2020, pH-responsive poly(gellan gum-co-acrylamide-co-acrylic acid) hydrogel: Synthesis, and its application for organic dye removal. *International Journal of Biological Macromolecules*, 153: 573-582.

Zhou, M, *et al*. 2013, Uniform hamburger-like mesoporous carbon-incorporated ZnO nanoarchitectures: One-pot solvothermal synthesis, high adsorption and visible-light photocatalytic decolorization of dyes. *Applied Catalysis B: Environmental*, 138-139: 1-8.

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