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Synthesis of a Green Adsorbent Surface Gels: Development of Ratio Preparation of Polymer SA/Bentonite Bead, and its Industrial Applications for Removal of Aqueous Pollutants

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Abstract: In this research, polymer gels sodium alginate/bentonite clay adsorbent beads (SA/Ben) were prepared via encapsulating natural bentonite (Bn) in sodium alginate (SA). The ratio of Polymer Gels SA/Bn was used during preparation bead to yield beads (1/1 w/w), SA-Bn2 (1/2 w/w), and SA-Bn3 (1/3 w/w), respectively. These adsorbents were characterized via different characterisation FESEM, TEM, XRD and EDX to give high confidence of the prepared surface. The adsorption of Clonazepam drug (CLZ) from aqueous solution on the SA/Bn beads was investigated as a function of different factors, including the initial concentration of CLZ, the weight of SA/Bn beads gel, pH solution, temperature of solution and equilibrium time. Adsorption models of Langmuir and Freundlich isotherms were applied and were found to be well described via the isotherm of Freundlich model. The results showed that among the three types of prepared surfaces SA/Bn beads, SA-Bn1 presented the greatest CLZ adsorption capacity. Thermodynamic parameters were calculated including change free of Gibbs energy (ΔG), change entropy (ΔS), and change enthalpy. The change enthalpy of CLZ drug adsorption was found to be positive for the SA/Bn bead and the reaction of adsorption spontaneous and exothermic. After the adsorption proses the SA/Bn beads can easily be regenerated via water and re-used within four cycles.

Key words: Clonazepam, polymer gels, bentonite**,** sodium alginate, adsorption, spontaneous.

Introduction

Adsorption is a popular method among these due to its advantages of being inexpensive, simple to use, more effective at treating the problem, available from various sources, and having a broad range of applications (Masoumeh 2022; Maria 2022; Mura 2000; Xinyou 2018). The adsorbent is a dependent cost component of drug adsorption due to the benefits of the adsorption method and the widespread distribution of the drug in aquatic settings. Therefore, it's critical to discover additional adsorbents that are affordable, effective, and environmentally friendly (Aljeboree 2023a; Hamadneh, 2015, 2021; Mura and Faucci, 2000; Syie, 2021; Vahid, 2023).

Clonazepam belongs to the benzodiazepine family and has a sedative and hypnotic effect. It is considered an antiepileptic as it affects chemicals in the brain that are unbalanced to treat seizures and certain types of anxiety disorders. The treatment may cause psychological and physical addiction, and it is not recommended to use it for long periods. Common side

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effects like drowsiness, dizziness, exhaustion, weakness in the muscles, memory problems, cough, runny nose or congestion, change in body weight, and blurred vision. Clonazepam is used to treat the following diseases Panic disorders and epileptic seizures (Masoumeh, 2022; Mura and Faucci, 2000).

Clay material bentonite is advantageous for adsorption due to its low cost and strong cation exchange efficiency. Additionally, it shares traits with other natural clays, namely a structure a crystalline and a small selection of functional groups (Alhattab, 2023; Ihaddadene, 2015; Khansili and Krishna, 2022; Mishra, 2018; Muhammad, 2020). Due to its abundant functional groups, nontoxicity, and eco-friendly attributes, sodium alginate (SA), a natural bio-polymer, has been usually employed as a gelling agent and binder for creating diverse composite materials for adsorption. Through crosslinking with calcium ions, SA creates a network of open interconnected pores. By encasing other adsorbents, it is simple to create composite beads. Because organically modified clay enhances drug removal, coating clay on a polymer enhances the efficiency of the prepared polymer to remove pollutants from wastewater. This work is a comparative to the literature survey (Asmaa, 2023; Mohammed et al., 2022) done and the results are shown in Table 1.

In the work, the adsorption capacity of CLZ drug by adsorption method utilising as an alternative adsorbent (polymer gels SA/Bn) was studied. Characterization analyses of SEM, XRD, TEM and EDX. After the adsorption proses the SA/Bn beads can easily be regenerated via water and re-used within four cycles.

Materials and Methods

Materials

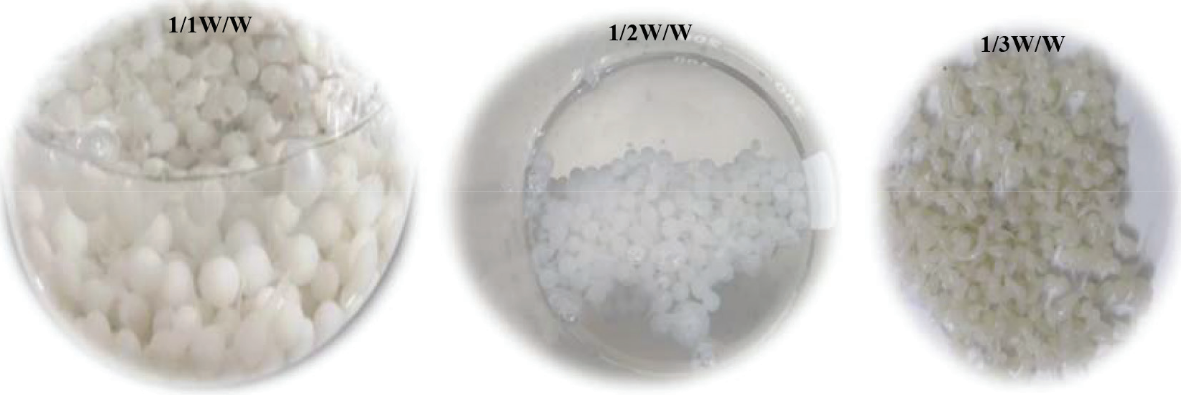
Sodium alginate, sodium hydroxide (NaOH) and hydrochloric acid (HCl), were purchased from Sigma Aldrich. The value pH solution was adjusted with 0.1 N M HCl or NaOH. Calcium chloride ($CaCl_2$), purchased from Shanghai, China, was utilised as cross-linkers.

Preparation of acid-activated bentonite clay

Bentonite Clay was obtained from the geological survey/Baghad/Iraq. Clay sample (bentonite) 20 g was soaked in 0.1N HCl acid in 100 mL overnight at 25^{o}C.

Table 1: Literature survey for removing of pollutants by using different surfaces

N.	*Sorbent*	*Pollutant*	*T (°C)*	*pH*	*t (hr)*	*Dose (g)*	*Q_e (mg/g)*	*E%*	*Co (mg.L^{-1})*	*Ref.*
1	SA-g-p(VFA-co-AAc)/ clay	Methylene blue	25	6	2	0.12	20.12	90	100	Hanif (2021
2	Chitosan/ Nano ZnO	Congo red	25	6	1	0.1	120	90	100	ALSamman (2021)
3	Alginate/acid activated bentonite beads (A-AAB)	Crystal violet	25	8	3	0.2	582.4	92	100	Akeem (2019)
4	Alginate/bentonite beads (AB)	Crystal violet	25	8	3	0.2	498.2	84	100	Akeem (2019)
5	PAM/SH/clay hydrogels	Methylene blue	30	6	1	0.05	180	86	20	Karim (2022)
6	Alginate/Mauritanian clay	4-nitrophenol	25	5.5	24	0.5	176	96	20	Abdelhahi (2011)
7	(SA-GO-Y) hydrogel	Tetracycline	**20**	**7**	**2**	**0.4**	**477.9**	**82**	**50**	**He (2020)**
8	(SA-g-p(VFA-co-AAc)\ BC) hydrogel	Methylene green	25	7	23	0.1	2108	-	200	Hanif (2021)
9	(SA-g-pAAc) hydrogel	crystal violet	25	7	1	0.05	333.33	-	250	Wared (2021)
10	SA-Clay -TiO2 NPs	Amoxicillin	30	4	1	0.05	198.8	85	100	Aljeboree (2023a)
11	SA-Clay -TiO2 NPs	4-chlorophenol	30	3.8	1	0.05	182.3	81	100	Aljeboree (2023a)
12	Polymer Gels SA/Bn	Clonazepam	25	6	1	0.1	71.22	95	30	In this study



Scheme 1: Preparation of Polymer Gels.

The sample acid-activated was washed thoroughly several times with DW until it shows neutral pH in normal solution and dried at 65°C in the oven.

Preparation of Polymer Gels Sodium alginate-bentonite beads (SA –Bn) clay

Sodium alginate solution (1g; V = 10 mL, 2g; V = 10 mL, and 3g; V = 10 mL) was prepared by drop-wise addition of NaOH into sodium alginate solution. the prepared sodium alginate solution was dissolved in distilled water, and Bentonite clay (1g in 10 ml, 4g in 10 ml, and 9 g in 20 ml) distilled water and mixture, stirring for 2 h. The homogenous solution mixture was filled into a syringe and dropped through the syringe needle into a flask having 100 mL of solution (3%, w/v) $CaCl_2$. After 12 h, the beads were collected from the solution and washed one by one by DW and dry to obtain powder use in the experiment.

Scheme 1: Preparation of Polymer Gels

Adsorption Experiments

All experiments of the adsorption study are carried out in a 100 ml conical flask containing SA/Bn beads gel with 100 ml CLZ drug solutions. Different parameters were taken for studying the effects of adsorption, such as equilibrium time (2-120) hr, the concentration of CLZ drug (5-40 mg/L), weight of SA/Ben beads gel (0.03-0.15 g), pH (2-11) and temperature (10-40°C), by using shaker control temperature for 60 min at 30°C. After the adsorption method attainment contact time, the solution of the drug was filtered and determined by UV–Vis spectrophotometer at a maximum of 272 nm. The percentage removal and adsorption efficiency of CLZ is calculated in equations 1 and 2:

$$\text{Removal Percentage } E\% = \frac{Co - Ce}{Co} \times 100 \quad (1)$$

$$\text{Adsorption capacity } Qe = \frac{(Co - Ce)V(\text{ml})}{W(\text{gm})} \quad (2)$$

Results and Discussion

Characteristics

Figure 1a shows the SEM image of bentonite clay. The analysis is performed to investigate the properties and morphology of the surface. In the picture, it can be seen that the clay has a lamellar and layered porous shape, which will increase the surface area, effective sites, and level of contact of the adsorbent with the pollutant, thus increasing the adsorption efficiency (Alhattab, 2023; Al Bakain, 2015).

To characterise the morphology of SA/Bn beads gel, shown in Figure 1b, the prepared polymer takes the shape of white balls, and many wrinkles and cavities can be observed on the surface of the polymer. This cavity-containing surface can raise the surface area among the adsorbent and adsorbate, thus increasing the adsorption efficiency of the polymer surface on the target drug (Hussain, 2022).

As for the surfaces after the adsorption process, polymer surfaces are shaped like “cauliflowers,” which are in the form of irregular grooves in the form of retinal folds with varying depths. These structural cavities in the surface help absorb contaminants (Raya 2021), as shown in Figure 1c.

Figure 2a is a TEM image showing the morphology of the surface polymer. The black cloud was more abundant and spread on the surface and a new geometry was created resulting from the surface loading of clay onto the surface bead gel, which may be attributed to the amount of clay on the bead gel. Figure 2b shows a TEM image of the polymer, where clay was observed embedded inside of the bead gel, too, incorporation

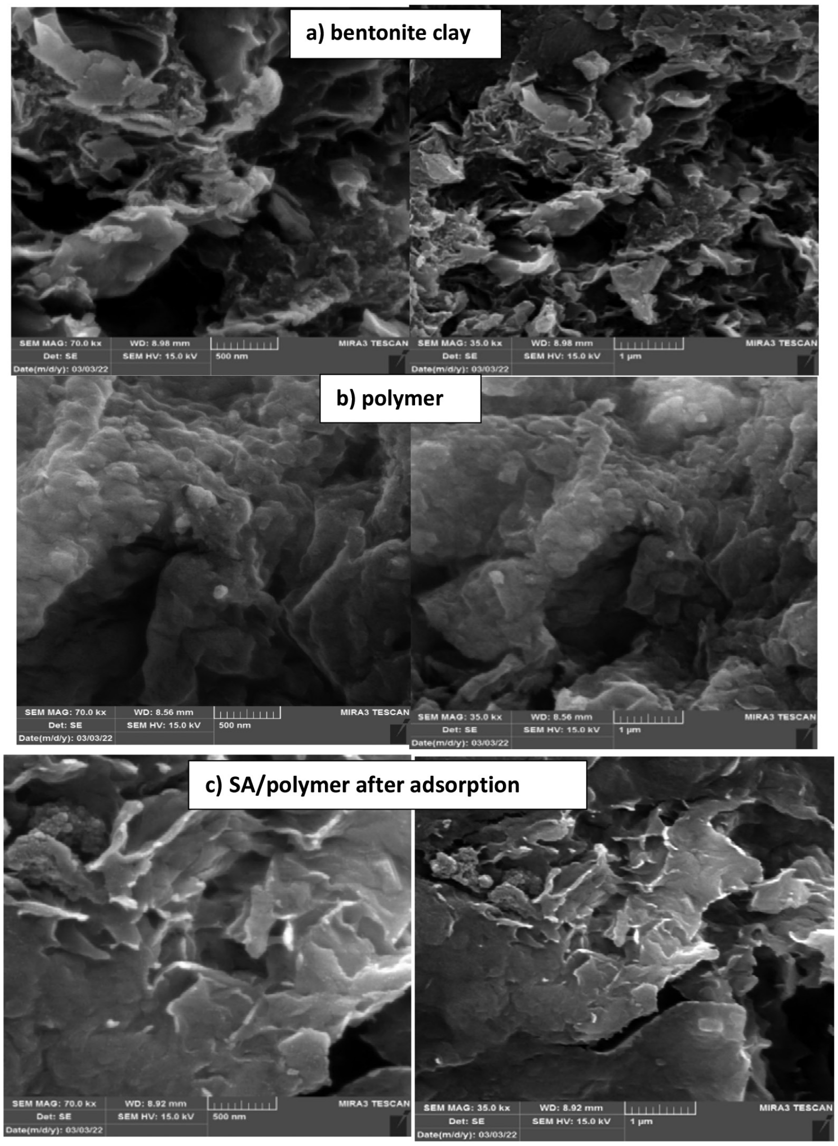


Figure 1: FESEM images at different magnifications of (a) clay, (b) polymer, (c) polymer after adsorption.

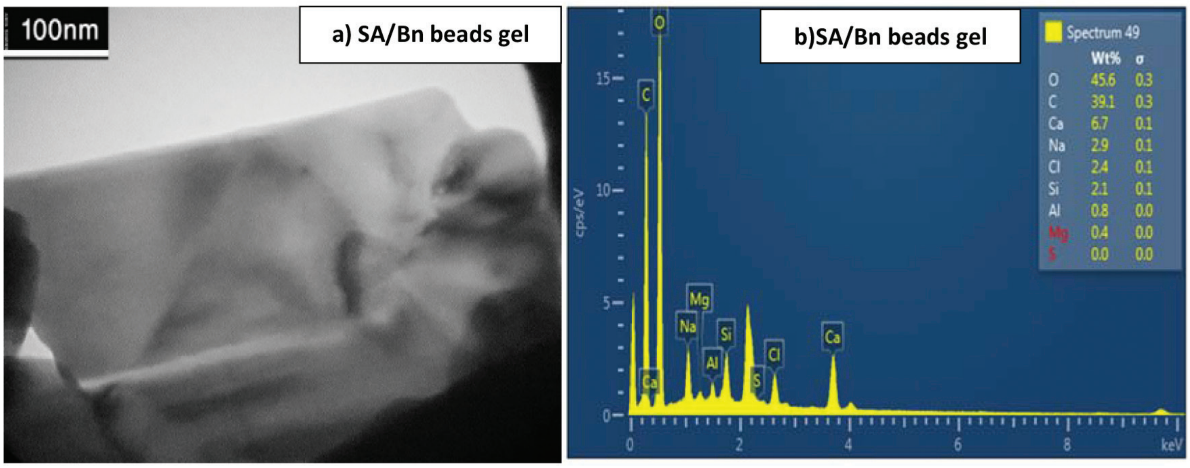


Figure 2: TEM image (a) polymer, (b) EDX spectrum of polymer.

of clay into beads gel is supported by the presence of elements (Mg, Al, Si, Ca and other elements). That indicates the presence of clay on to bead gel. values of the lowest and highest elements that existed in the modified SA/Bn beads gel 0.4- 45.6 Wt.% (Alhattab, 2023; Fatemeh, 2022).

In Figure 3, the properties of the polymer were acquired utilising X-ray. The XRD pattern of polymer have two peaks, one peak at 20.5 degrees, which is related by the crystalline structure hydrated, and two peaks at 38.1 degrees, which is associated with an amorphous called semi crystalline structure (Abdulrazzak, 2021).

Effect of Dose SA/Ben Beads Gel

The effect of dose polymer (0.03– 0.15 mg) on removal percentage % of CLZ drug at a concentration of 30 mg/L as shown in Figure 4. As shown in the figure, increases the removal of drug with an increased weight of polymer until a certain limit 0.1 g and then, the rate show slowly change in decreasing. At the initial stage, a rapid increase in the adsorption with the rise of mass polymer can be ascribed to a larger surface area and the availability of more sorption sites. After this vital weight of 0.1 g, the number of active sites rises with a slower adsorption rate due to the shortage of adsorbate in the solution. The E% increases at increased weight polymer due to rapid superficial adsorption onto the composite surface, leading to a smaller solute concentration in the solution than a lower polymer dose (Alhattab, 2023; Hemant, 2021).

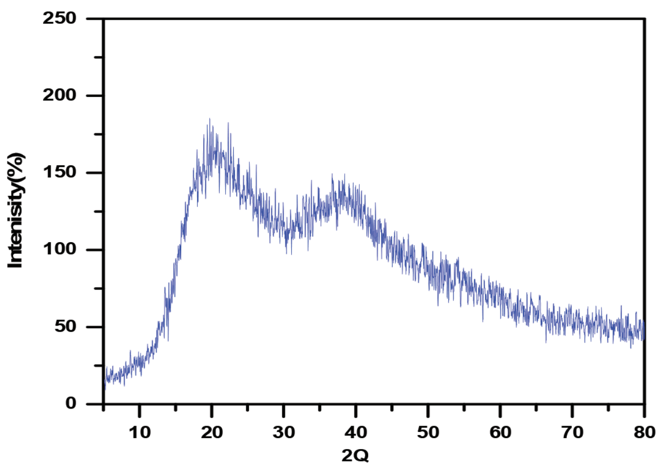


Figure 3: XRD of polymer surface.

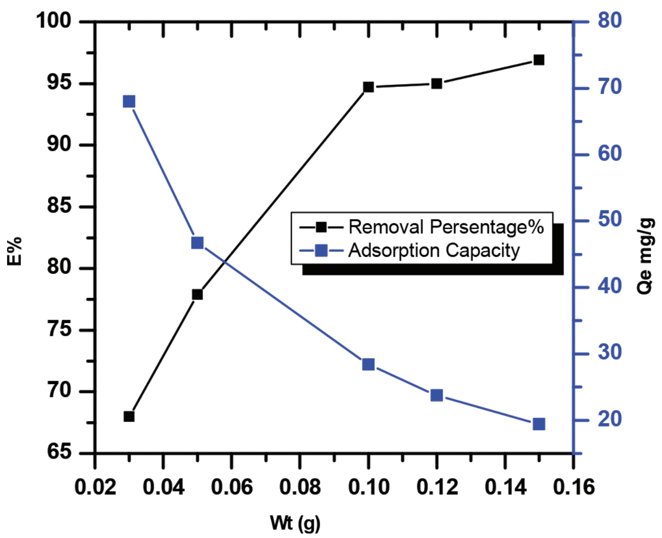


Figure 5: Effect of dose polymer on adsorption capacity and removal percentage % of CLZ drug.

Effect of Solution pH

The effect of pH solution is very important to the removal of CLZ drug via polymer, As can be seen from Figure 5, drug E % was found to increase with the rise in pH solution and the data obtained from the replicates for each pH solution were quite consistent (Yan, 2022). In this study, the best drug removal was achieved at solution pH 11, with removal of a maximum of 92.93%, at 30 mg/L of drug. The equilibrium adsorption efficiency of the drug onto polymer is very small in the acid medium at pH 2. The adsorption efficiency (Qe mg/g) of pH 2 (14.33 mg/g), suggests that polymer is an excellent adsorbent for the removal of drugs from large volumes of aqueous solutions. When the solution pH is more than 7, the adsorption efficiency (Qe mg/g) of the drug onto the polymer increases with increasing solution pH. Lower removal of the drug in the acidic medium is possibly due to the presence of excess H^+ ions competing with the cation groups on the drug for adsorption sites. At large solution pH, the polymer may get positively charged, which enhances the negatively charged drug through electrostatic forces of attraction (Karim, 2022; Mohamed, 2020; Zhuqing, 2019).

Effect of solution temperature and studied thermodynamic parameters

The influence of solution temperature on the adsorption process was studied in a wide range (10-40°C), with results shown in Figure 6. It can be seen that the adsorption capacity drug decreases with increased solution temperature. The decrease in adsorption capacity via increasing solution temperature means the polymer acted as an adsorbent in the exothermic process, and the mass transfer at heating up to a temperature higher starts and separated drug molecules from the solid surface of the adsorbent (Dijana, 2016; Mohamed, 2020; Karim, 2022).

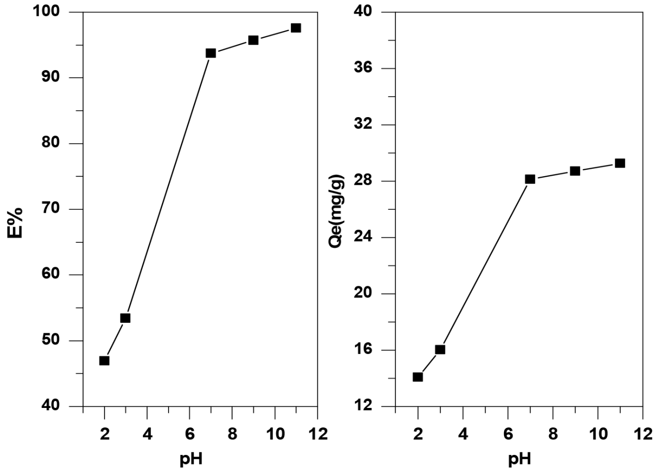


Figure 5: Effect of pH solution onto removal of CLZ drug by polymer.

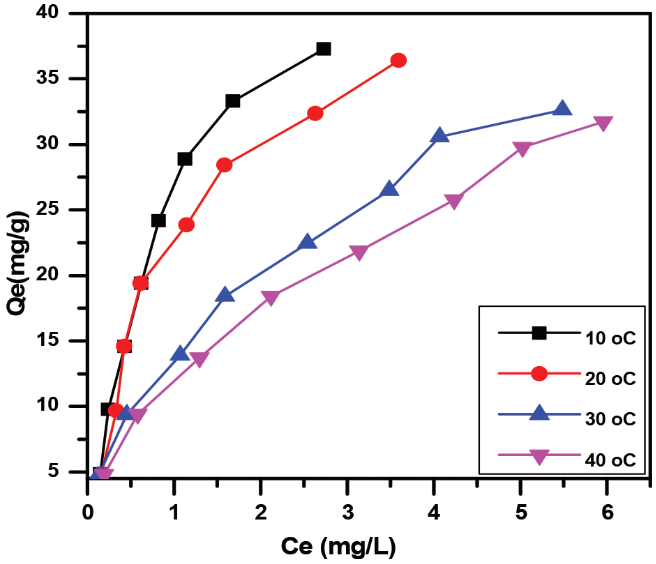


Figure 6: Effect of several temperature solution onto removal CLZ drug.

The thermodynamic factors counting change in enthalpy ΔH, Gibbs free energy ΔG, and change in entropy ΔS and the equilibrium constant (K_e) of the adsorption method were calculated via utilising equations :

$$\Delta G = -RT \ln K_e \quad (3)$$

$$K_e = \frac{(Q_{\max})*Wt\,(gm)}{(Ce)*V(L)} \quad (4)$$

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

when $X_{m:}$ is the maximum value of adsorption at a certain value of concentration equilibrium (Ce mg/L). Table 2 lists the values X_m at several solution temperatures drug. Plotting ln X_m vs. 1/T should produce a straight line with a slope –ΔH/R as shown in Figure 7. The value of ΔH and ΔS can be determined from the slope and intercept in the same order (Al-Dujaili, 2012; Honglin, 2023)

Table 2: Maximum adsorption amount value X_m CLZ drug on to polymer

T(K)	*1000/T(K^-1)*	*C_e = 2.8*	
		X_m	*ln X_m*
283	3.5335	36.5	3.5973
293	3.4129	32.1	3.4688
303	3.3003	22	3.0910
313	3.1948	19	2.9444

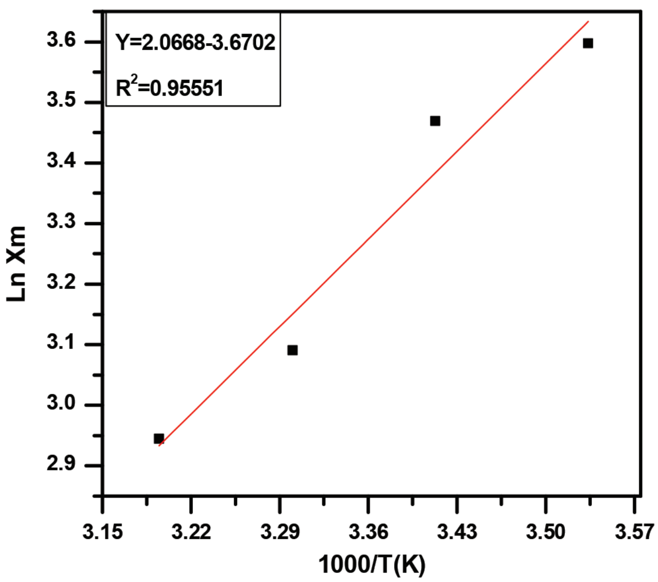


Figure 7: Plot ln X_m Vs. absolute temperature of the adsorption CLZ on to polymer.

From the data given in Table 3, the change enthalpy ΔH and change entropy ΔS for adsorption are assumed to be solution temperature independent. The value of change enthalpy ΔH exothermic and ΔG spontaneous negative value of the adsorption is a measure of the energy barrier that must be overcome via reacting molecules. While value ΔS positive of CLZ drug refers to a random system (Hameed, 2008; Honglin, 2023).

Adsorption Isotherm

This adsorption isotherm explains the behaviour of the adsorption process, which determines the adsorption capacity from the amount of the adsorbed substance (CLZ drug) to the amount of the adsorbed substance polymer in equilibrium. Adsorption isotherms were

Table 3: Thermodynamic parameter of CLZ drug on the polymer

Thermodynamics parameters T/K	*ΔG/ kJ.mol^{-1}*	*ΔH/ kJ.mol^{-1}*	*ΔS/ J.K^{-1}. mol^{-1}*	*Ke*
283	-6.0414	-17.183	-30.512	13.035
293	-5.94198			11.464
303	-5.1933			7.8571
313	-4.9829			6.7857

studied to determine adsorption efficiency, and each isotherm utilised has special assumptions. Freundlich isotherm and Langmuir isotherm models were applied (Aljeboree, 2023b).

Langmuir Isotherm Model

Langmuir isotherm model depends on the behaviour of the mono-layer adsorbed on the solid surface of the adsorbent, and the adsorption energy is also distributed evenly on the solid surfaces (adsorbents). Significant factors that must be determined are the factors in the Langmuir isotherm (Mohammed, 2018): the maximum adsorption at equilibrium and the adsorption rate. The Langmuir isotherm model equation is non-linear as calculated in Eq. 6:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{6}$$

Freundlich Isotherm Model

The Freundlich isotherm model is based on an experimental equation to analyse the adsorption capacity and adsorption rate on homogeneous surfaces of the adsorbent, and the Freundlich isotherm also depends on the mechanism of adsorbed multilayers instead of monolayer surfaces as in the Langmuir isotherm (Honglin, 2023). The Freundlich isotherm equation calculates in Eq 7:

$$q_e = K_f C_e^{1/n} \tag{7}$$

Theoretical and experimental results indicate that the hydrogel isotherms are shown in Figure 8, and their correlation coefficients are presented in Table 4. Based on the values of (R^2), it can be concluded that Freundlich isotherm was the best CLZ drug model Isothermal bio sorption of the hydrogel, thus shedding light on the occurrence of multilayer adsorption in this process. Besides, the model Freundlich constant (1/n) is 0.472 for the CLZ drug, revealing that the adsorption method was favourable (Arami, 2006).

Table 4: Adsorption model of CLZ drug onto polymer

		Polymer
Freundlich	K_f	20.845
	1/n	0.472
	R^2	0.9887
Langmuir	q_m (mg/g)	46.087
	K_L (L/mg)	0.987
	R^2	0.9233

Reactivation and Regeneration and of SA/Ben Beads Gel

The reuse of polymer, after adsorption, is one of the important economic parameters for the treatment way. It helps in elucidating the mechanism of removal of drugs from drug-loaded adsorbent, reactivation mechanism and regeneration of spent adsorbents, which in turn may reduce operational costs and protect the environment from secondary contamination. Drug desorption studies were carried out by means of several desorption agents for example (0.01N) NaOH, HCl and H_2O. The polymer was reactivated and regenerated completely (i.e., 100%) by using HCl. This is because in acidic solutions -COO$^-$ is converted into –COOH, and correspondingly, the electrostatic interactions among polymer and drug are weakened. The reuse of polymer via utilising solution HCl in the drug adsorption method was studied up to 4 cycles under the best conditions. After the four cycles of utilised SA/Ben beads gel, the removal percentage

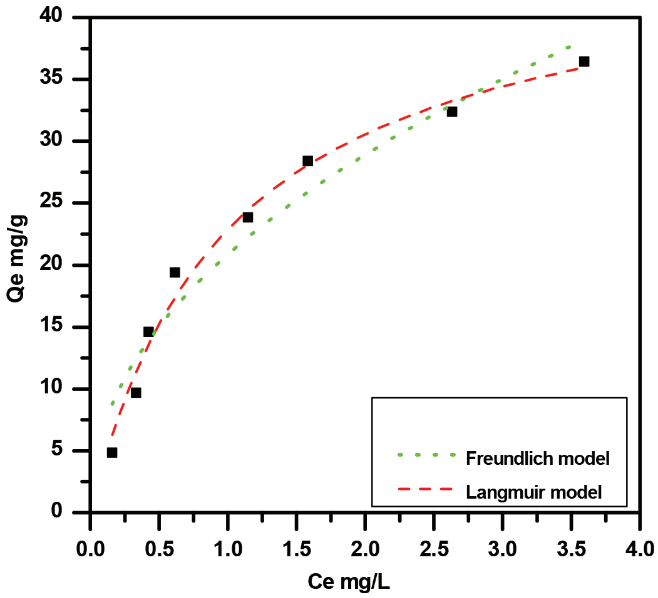


Figure 9: Adsorptions isotherm models non-linear fit of adsorption CLZ drug onto polymer.

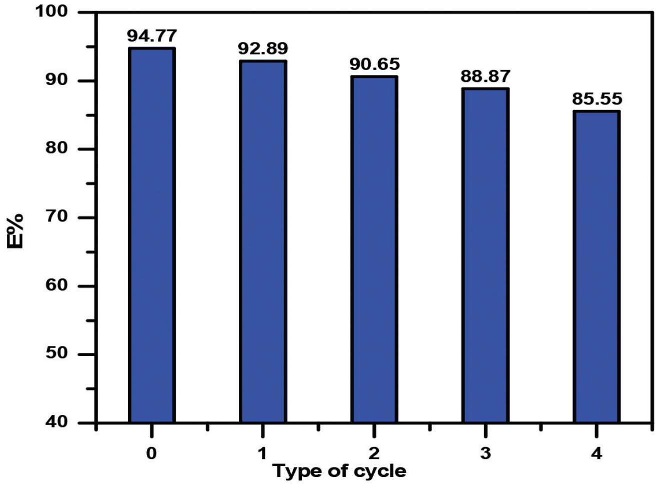


Figure 10: Effect of type number cycle of SA/Ben beads gel.

(>90%) shows polymer is a possible renewable absorber (Alhattab, 2023; Syie, 2021) as appears in Figure 10.

Conclusion

In this study, polymers were successfully synthesised (SA/Bn) by utilising a simple one-step synthesis process. SA-based beads were synthesised via both modified and conventional processes, and bentonite clay was well encapsulated inside the SA beads. With the modified way and the clay encapsulated, the beads have large pore structures. Therefore, SA/Bn can remove 94.2% and maximum adsorption efficiency of 82.88 mg/g. The values ΔH and ΔS for adsorption are assumed to be solution temperature independent. The ΔH of the adsorption is a measure of the energy barrier that must be overcome via reacting molecules, the reaction is exothermic. Polymer can be regenerated by acid washing while maintaining the efficiency of the prepared polymer in removing contaminants in the process of repeated use for 4 cycles. Due to the use of materials prepared with polymers that are easily available, inexpensive and environmentally friendly, the prepared polymers are considered to have a very high efficiency in removing pollutants compared to industrial polymers. From the isotherm adsorption models, further considering the study proofs, and best-fitted model Freundlich, and the changes structural induced via synthesis and addition clay played a key role in more improvement to remove pollutants.

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