RESEARCH ARTICLE

Synthesis and Characterization of Poly (CH/AA-co-AM) Composite: Adsorption and Thermodynamic Studies of Benzocaine on from Aqueous Solutions

Abbas N. Karim, Layth S. Jasim

Department of Chemistry, College of Education, University of Al-Qadisiyah, Iraq

Received: 13th Oct, 19; Revised: 15th Nov, 19, Accepted: 15th Dec, 19; Available Online: 25th Dec, 2019

ABSTRACT

The research includes the preparation of cross-linking hydrogel (polo (CH-(AAc-co-Am). The method; polymerization of the free radicals by using the Chitosan as initiator for the reaction, also with the help of karnofsky score (KPS) and TEMED as cofactors. The mixture gets treated by Acrylic acid and Acrylamide that include MBA as a cross-linking agent. The adsorption was proved by using the fourier-transform infrared spectroscopy (FT-IR) and field emission scanning electron microscopy (FE-SEM)analysis. In addition, TGA showed that the hydrogel is stable in high temperatures.

The thermodynamic study of the hydrogel was performed by using the Benzocaine Drug, which includes measuring the Entropy and Enthalpy and Chips energy. It also showed that the hydrogel is governed by Freundlich and Temkin equations, and the adsorption from the Pseudo-second order model. The adsorption is a Physical and Exothermic. The adsorption time was 120Minutes.

Keywords: Adsorption, Benzocaine, Desorption, Hydrogel, Polymer.

International Journal of Drug Delivery Technology (2019); DOI: 10.25258/ijddt.9.4.8

How to cite this article: Karim, A.N. and Jasim, L.S. (2019). Synthesis and Characterization of Poly (CH/AA-co-AM) Composite: Adsorption and Thermodynamic Studies of Benzocaine on from Aqueous Solutions. International Journal of Drug Delivery Technology, 9(4): 558-562.

Source of support: Nil.

Conflict of interest: None

INTRODUCTION

Polymers considered to be the primary component in new developing technology. The Polymers flexibility, lightness, and ability to carry heavy weight made it replaced many synthetic materials like wood and metal.[1] Additionally, the Cross-linked Polymers, Hydrogel, in particular, have a very useful function in regulating drugs and preventing Drug poisoning. Studies in the United States and Sweden in 2013 showed as many as 43982 death in drug overdose or alcohol.[2,3] to avoid some of the unintended consequences (Overdose) of some drugs, researchers started to use hydrogel to regulate the release of the medicine in the body is controllable, measurable doses.[4] The method of adsorption has many benefits most importantly, it is used to act as an antibacterial,[5] water purification,[6] measuring electrical Conductivity and the effect of adsorption in some solutions,[7] measure the water pollution,[8] abstract heavy metals,[6,9] extraction of metal mud in the petroleum excavation operations,[10] Chromatography applications,[11] and many technological uses.[12]

EXPERIMENTAL

Chemicals and materials

Acryl amide and Acrylic acid ware supplied by (Himedia, India). The activated N,N,N',N'-tetra methyl ethylene diamine (TEMED) was also supplied by (Himedia, India), The initiator, potassium persulfate (KPS) was supplied by (Merck, Germany). The multifunctional crosslinker is N, N'-methylene bisacrylamide (NMBA) was purchased from (Fluka, Germany). Sodium chloride was obtained from (Alpha Chemika). Benzocaine was purchase from (Sigma-Aldrich, Germany). Sodium Hydroxide and Hydrocholric acid were supplied from (Fluka, Germany).

Preparation of poly (CH-(AAc-CO-Am))

To prepare hydrogel (CH/AA-CO-AM))[13,14] we prepare two solutions as following:

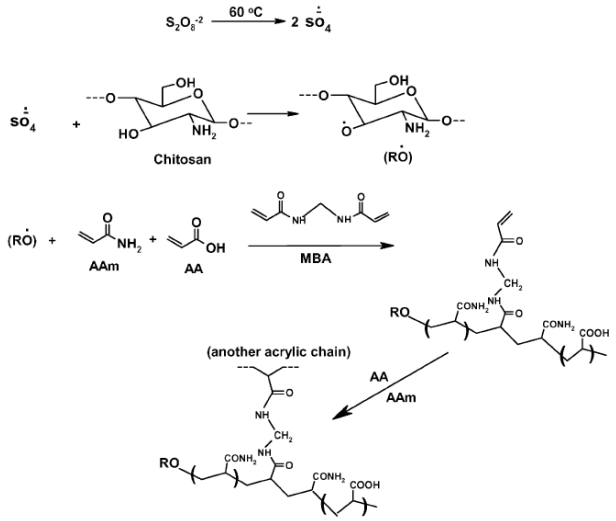
First Solution: add (6g) of Acrylic acid to Sodium Hydroxide. Then add the Acrylamide (6 g. In 10 mL water) and MBA in concentration (0.05gm. in 5 mil water). Leave the mixture for stirrer for 15 minutes.

Second solution: put (1g) of Chitosan in acetic acid (2%) on the stirrer for 15 minutes at a 60^{o} add KPS (0.1 g) In 5mL water and TEMED (0.05g in 5 mL water. Now add the first solution to the second drop by drop in 50^{o}. leave it in bathwater for two hours to produce the hydrogel (Scheme 1).

Adsorption Isotherm

Solutions of drug (10 mL) from (1–50 ppm) at pH 1.2 were added to the closed bottles containing 0.05g of hydrogel. Put

**Author for Correspondence: layth.alhayder@gmail.com*



Scheme 1: The formation of Hydrogel equation 15

all the solutions in the shaker in a thermostatically controlled water bath and start stirring for equilibrium time at 120 min The end is the separation of the solutions by the centrifuge for 15 min at 6000 rpm to calculate the absorbance after adsorption by using a UV-Visible spectrophotometer.

The quantity of drug adsorbed qt and the removal percent of the drug was determined by the following equations.[16]

$$Q_e = \frac{(C_o - C_e) \times V_{sol}}{m} \quad (1)$$

$$Adsorption\ \% = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

Where C_o and C_t are the initial and equilibrium concentrations of drug in the solution in mg/L, respectively, m is the mass of hydrogel in mg. V is the volume of the solution.

Effect of Temperature

To study the thermo effect on the adsorption of Poly (CH-(AAc-CO-Am)), multiple concentrations (1-50) mg/L was prepared. Also, all conditions (pressure, drug volume, the adsorption surface) constant in all experiments. The test sample was placed in a shaker for 120 minutes in different temperatures (5,15,20)°. The concentration was measured by UV-VIS spectrum after it was separated by centrifuge and with the use of Micro Syringe.

Effect of pH

We used a pretreated solution with a pH from (1.2 to 10 (10ml samples). We mixed in room temperature, drug concentration of (20mg/l), and composite (Poly (CH-(AAc-CO-Am)) of (0.05 g) with the hydrogel for 120 minutes. We then separate the solutions by centrifuge and extract the sample by microsyringe and measure the adsorption by using UV-VIS Spectrum

Effect of Ionic Strength

A solutions ware used with a different salt (CaCO3, KCl, and NaCl) in variety of concentrations (from 0.001g. to 0.2 gm.), and a sample size of (10ml) was put in the shaker for 120 minutes and separated in the centrifuge (600rpm) for 15 minutes. The solution was extracted by a microsyringe and measured by UV-VIS spectrum.

RESULTS AND DISCUSSION

Characterization

The analysis was done by Ft-IR for AAc-co-Am (Figure 1) and Poly (CH-(AAc-CO-Am)) (Figure 2) below. At (3210 cm^{-1}) shows the Hydroxyl, which intersects with (3356cm^{-1}) the amine group due to the Hydrogen bond. Also, at (2939 cm^{-1}) is the alkyl. At (1651 cm^{-1}), the carbonyl in the amide appears. As for (1720 cm^{-1}), the carbonyl in the carboxyl. At (1272 cm^{-1}), the bond between the nitrogen and the carbon.[17]

After adsorption: there are no adsorption bonds detected beyond (3000 cm^{-1}) as a comparison to the Hydrogel analysis (Figure 3).

Using FE-SEM analysis shown that Hydrogel Poly (CH-(AAc-co-Am)) has a smooth surface. The surface contains many layers those are compacted on top of each other by Vander Walls force and the cross-linking agent. After the

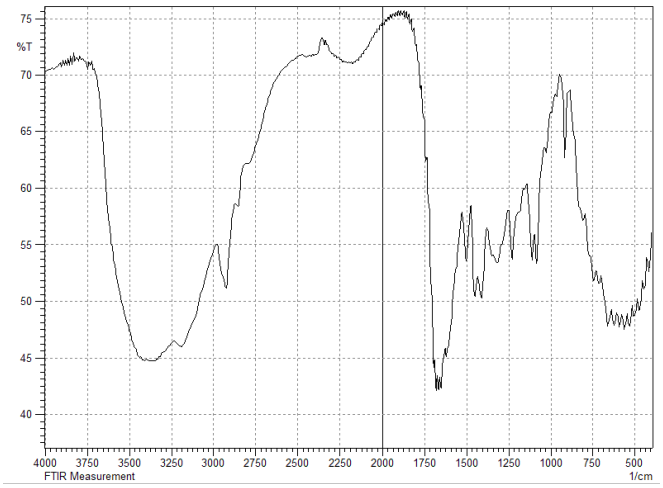


Figure 1: FT-IR Analysis of Poly (CH-(AAc-co-Am))

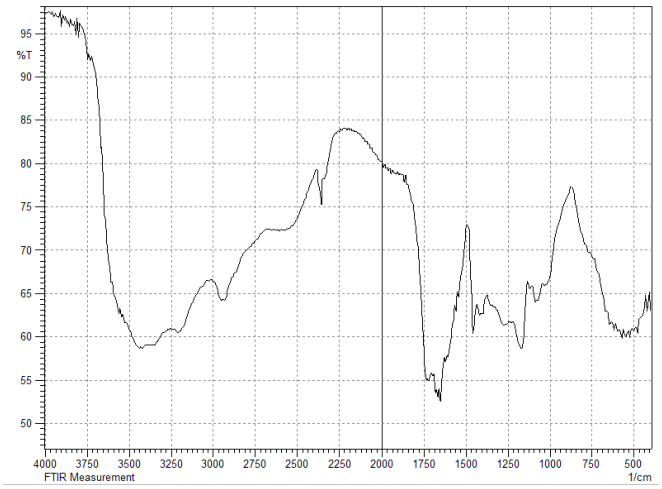


Figure 2: FT-IR Analysis of Poly (CH-(AAc-CO-Am))

adsorption the surface is shown to be bumpy. The bumps on the surface, mostly from Benzocaine (Figure 4).

A Study of the Hydrogel Poly (CH/AAc/AM) was conducted by using TGA technology. The study revealed, and as it is showing in Figure 5 that the hydrogel is stable in the temperature similar to the human body temperature (37°C), the hydrogel also continue to be stable to 211.82°C The Hydrogel will start to decompose slowly in higher temperature and by 8.783% until reaching 324.06°C where all it remains is 74.261%. This could be a result of the decomposition of the Amide and Hydroxyl group in the hydrogel. At 500.77°C, the hydrogel will be decomposed completely, leaving the compound that adsorbed by it intact.

Adsorption Experiments

Effect of adsorbent weight

The deferent weight of hydrogel was taken (0.001-0.1 g), and put it in constant concentration from Benzocaine Drug (20

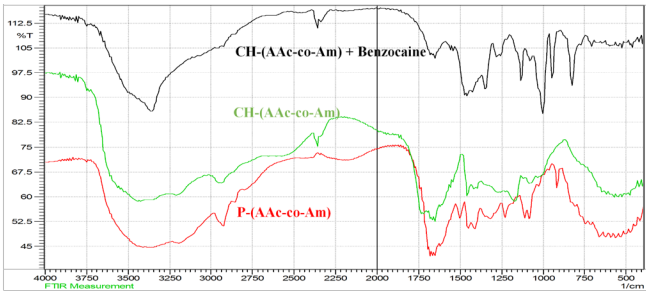


Figure 3: FT-IR analysis for Poly (CH-(AAc-co-Am)) after Benzocaine Adsorption

mg/L) with volumes (10ml), to determine the effective weight for adsorption left all samples 120 min to equilibrium and separated all solutions to measure the adsorption, then the adsorption found increased with increase of weight of hydrogel because of the increasing of functional group intel (0.05g) after that the Adsorption is Approximately constant because the solution is saturated (Figure 6).

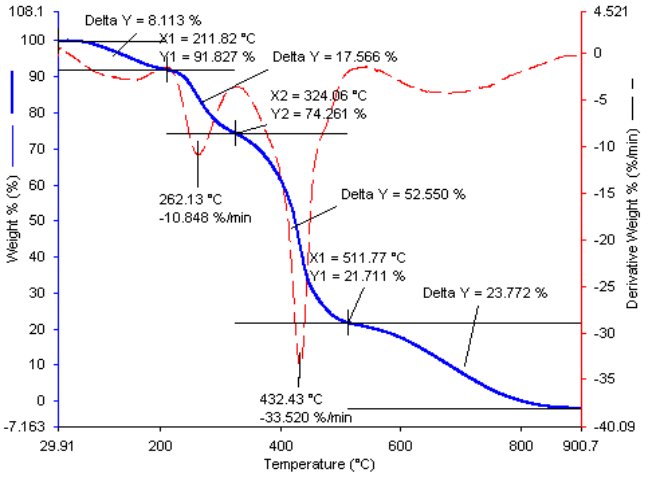


Figure 5: The carve of stability for Poly (Ch-(AAc-CO-Am)) By Using TGA

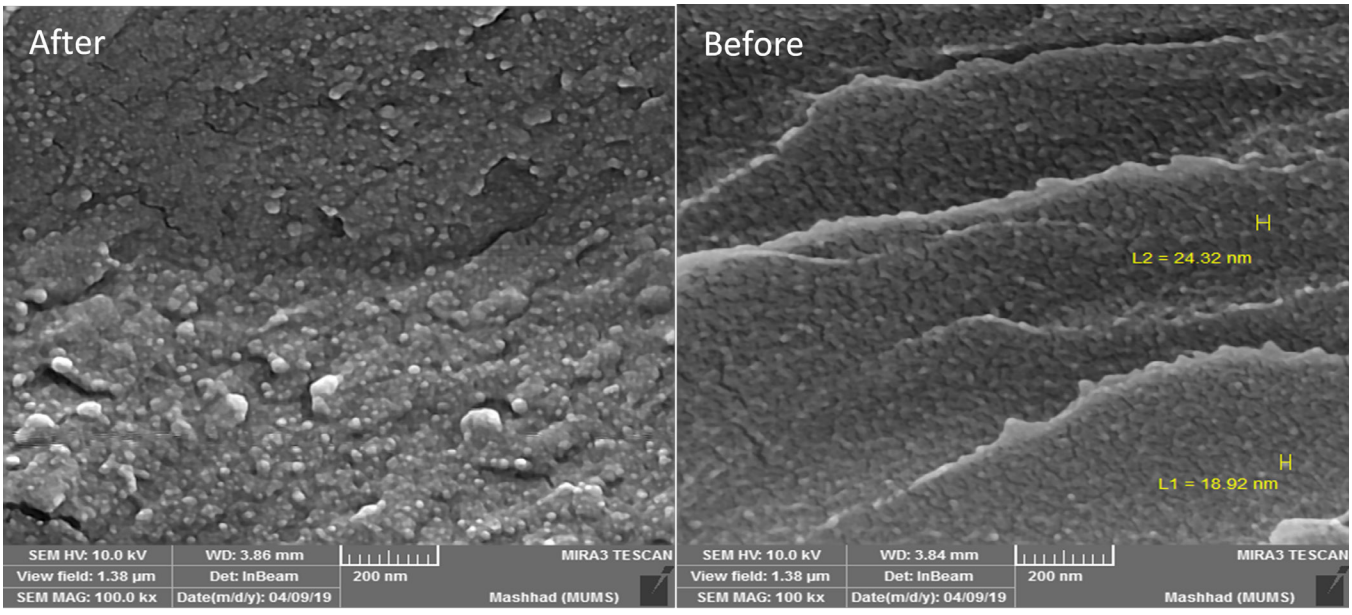


Figure 4: FE-SEM for Poly (CH-(AAc-co-Am)) after and before adsorption

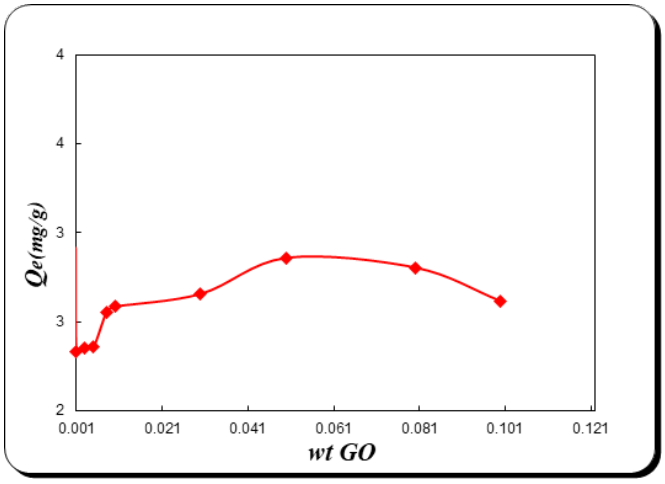


Figure 6: Effect of Hydrogel weight for Benzocaine Adsorption

Effect of temperature and calculation of thermodynamic functions

The thermodynamic study shows that the adsorption increases with the decrease of temperature, which means that the reaction is Exothermic (Figure 7). The reason for that phenomenon is that the Benzocaine Kinetic energy increase with the increase in temperature. The very active Benzocaine moves back and forth between the hydrogel to the solvent (water), which decreases the amount of Benzocaine in the hydrogel. If we compare the concentration of Benzocaine at 5ºC (409mg/L) and at 30ºC (1118 mg/L), you can see that the temperature has a negative effect of the adsorption process for the Benzocaine and Hydrogel in higher temperature.[18]

By studying the adsorption and Temperature correlation, we were able to study the enthalpy for Benzocaine on the Hydrogel surface, which equal to -32.6 KJ/mol. The negative means that the reaction is Exothermic and the adsorption is Physical (40KJ/mol) (Table 1).

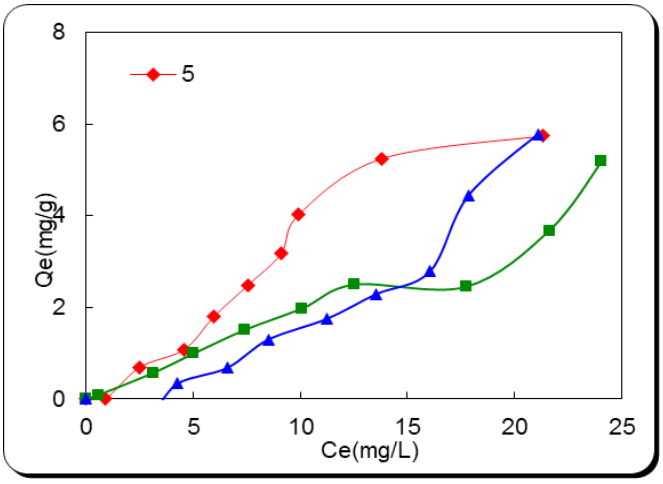


Figure 7: Effect of Temperature on the removal percentage of Benzocaine

Effect of pH

A study of the acidic effect on the adsorption revealed that the adsorption increases with the increase of acidic (Lower pH) (Figure 8), this led to many conclusions, one of which, that Benzocaine that contains ammine group (protonation constant of pk = 2.5). That Ammine gets converted to the positive ammonium ion that has a static attraction toward the negative groups on the surface of the Hydrogel (Carbonyl and carboxyl). Also, the decreasing pH increases the adsorption due to ionization of ammine groups on the Hydrogel Poly (CH-(AAc-co-Am)), which give them the positive that attract the aster groups on the Benzocaine.[14,19]

Effect of Ionic Strength

It was noticed that adsorption increases by increasing the amount of sodium or Potassium Chloride. Also noticed that calcium carbonite has a negligent effect on the adsorption. As it is shown in (Figure 9). The increase in adsorption with the increase of the sodium or Potassium Chloride due to the effect of the salt on the Hydrogel surface. The increase in these salts creates a negative charge on the top of the surface. The negative charge from the salt pushes the Benzocaine and hydrogel closer, which leads to higher adsorption.[20] As of the calcium carbonate, the positive charge on the calcium Ca^{+2} composes a complex with the negative part of the Benzocaine, which makes the adsorption less likely.[21]

CONCLUSIONS

- The CH/AA-CO-AM composite appeared of the highest activity in the adsorption from a solution of the drug.
- Due to the higher activity of composite in adsorption of the drug, it may be used as an antidote for the treatment of acute poisoning by Benzocaine.

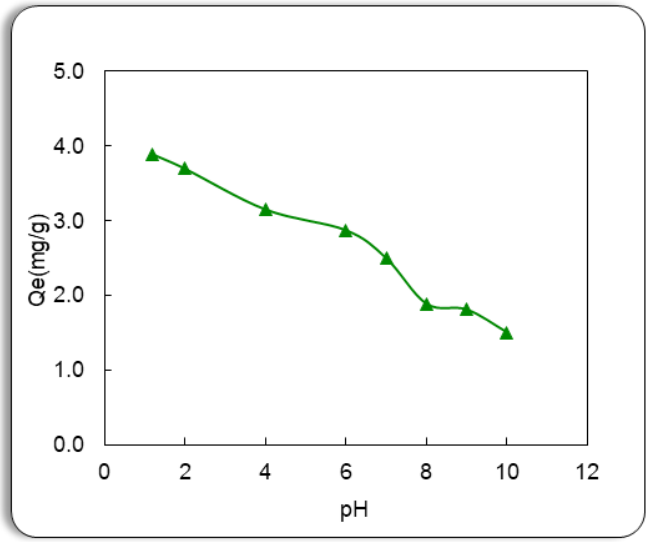


Figure 8: Effect of pH solution on Adsorption on Benzocaine

Table 1: Thermodynamic parameters of Adsorption for Benzocaine on surface

ΔH (KJ.mol^{-1})	ΔG (kJ.mol^{-1})	ΔS (J.mol^{-1}.K^{-1})	Equilibrium constant
-32.600	-3.296	-100.015	0.946

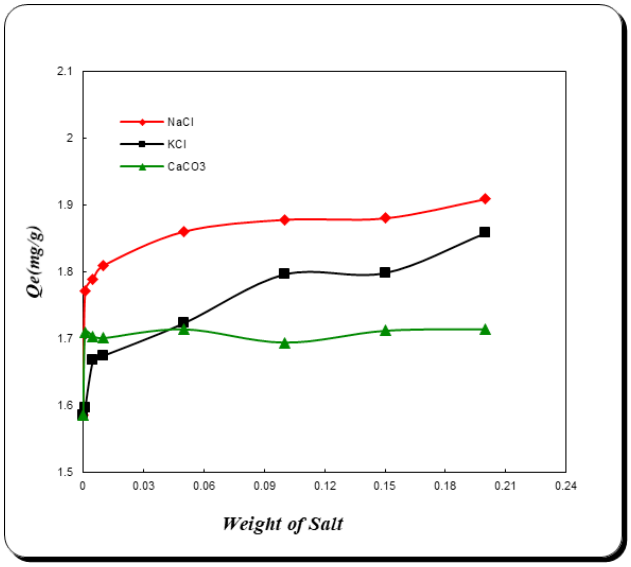


Figure 9: Effect of ionic strength on benzocaine adsorption

- The adsorption isotherms of Theobromine on attapulgite and bentonite obeyed Freundlich isotherm.
- benzocaine-composite reactions exhibited high enthalpy values (endothermic).
- Adsorption of the drug on the composite was pH-dependent.
- There was a positive correlation between the amounts of Benzocaine adsorbed and the ionic strength of solution.

REFERENCES

1. Okele, A. I. (2017). An Introduction to Polymers and Some Profiles of Polymer Industries in Nigeria. *SF J Polymer Sci*, 1(1), 3-6.
2. Hedegaard, H., Chen, L. H., & Warner, M. (2015). Drug-poisoning deaths involving heroin: United States, 2000-2013 (No. 190). US Department of Health and Human Services, Centers for Disease Control and Prevention, National Center for Health Statistics.
3. Jones, A. W., Kugelberg, F. C., Holmgren, A., & Ahlner, J. (2011). Drug poisoning deaths in Sweden show a predominance of ethanol in mono-intoxications, adverse drug–alcohol interactions and poly-drug use. Forensic science international, 206(1-3), 43-51.
4. Chai, Q., Jiao, Y., & Yu, X. (2017). Hydrogels for biomedical applications: their characteristics and the mechanisms behind them. Gels, 3(1), 6.
5. Fan, W., Wu, D., Tay, F. R., Ma, T., Wu, Y., & Fan, B. (2014). Effects of adsorbed and templated nanosilver in mesoporous calcium-silicate nanoparticles on inhibition of bacteria colonization of dentin. International journal of nanomedicine, 9, 5217.
6. Ku, Y., & Peters, R. W. (1987). Innovative uses from carbon adsorption of heavy metals from plating wastewaters: I. Activated carbon polishing treatment. Environmental progress, 6(2), 119-124.
7. Al-Niemi, K.I., Al-Dboone, S.A., and Abd-Algane, T. (2011). *Effect Of Using MnO_2 As Adsorbant On The Ionization Constant And Electrical Conductivity For Some Aliphatic Carboxylic Acid Containing By Hydroxyl Group On A- Position* Journal of University of Anbar for Pure science. **5**(3): p. 49-63.
8. A. Abd, F., Noor, S.A.A. and Al-Shamri, A.M.J. (2011). Measurements Of Mineral Waters Pollution In Adsorption Thermodynamic Study 0F Berlent Green Dye On Surface Bentonite Clay Bentonite. Journal of University of Anbar for Pure science. **5**(1): p. 61-70.
9. Zhang, J., Wang, A.J.J.o.C. and Data. E. (2010). Adsorption of Pb (II) from aqueous solution by chitosan-g-poly (acrylic acid)/attapulgite/sodium humate composite hydrogels. **55**(7): p. 2379-2384.
10. Bashi, A.M., Hadawi, S.M. and Ali, J.H. (2007). Extract new catalysts from mineral clay as substitutes for adsorption and thermal crushing operations in oil refineries. Journal of Kerbala university. **5**(2): p. 81-86.
11. Chase, H.A.J.T.i.B. (1994). Purification of proteins by adsorption chromatography in expanded beds. **12**(8): p. 296-303.
12. Crittenden, B. and W.J. Thomas. (1998). *Adsorption technology and design*. Elsevier.
13. Cheng, B., *et al*., (2017). Advances in chitosan-based superabsorbent hydrogels. **7**(67): p. 42036-42046.
14. Povea, M.B., *et al*., (2011). Interpenetrated chitosan-poly (acrylic acid-co-acrylamide) hydrogels. Synthesis, characterization and sustained protein release studies. **2**(06): p. 509.
15. Mahdavinia, G., *et al*., (2004). Modified chitosan 4. Superabsorbent hydrogels from poly (acrylic acid-co-acrylamide) grafted chitosan with salt-and pH-responsiveness properties. **40**(7): p. 1399-1407.
16. Makhado, E., *et al*. (2018). Preparation and characterization of xanthan gum-cl-poly(acrylic acid)/o-MWCNTs hydrogel nanocomposite as highly effective re-usable adsorbent for removal of methylene blue from aqueous solutions. Journal of Colloid and Interface Science. **513**: p. 700-714.
17. Wang, Q., Zhang, J., and Wang, A.J.C.P. (2009). Preparation and characterization of a novel pH-sensitive chitosan-g-poly (acrylic acid)/attapulgite/sodium alginate composite hydrogel bead for controlled release of diclofenac sodium. **78**(4): p. 731-737.
18. Allen, J. L., *et al*. (1994). Solubility of Benzocaine in Freshwater. Vol. 56. 145-146.
19. Kara, F., *et al*., (2006). Immobilization of urease by using chitosan–alginate and poly (acrylamide-co-acrylic acid)/κ-carrageenan supports. **29**(3): p. 207-211.
20. Al-Heetimi, D.T.A., Kadhum, M.A.R. and O.S.J.J.o.A.-N.U.-S. Alkhazrajy, (2014). Adsorption of Ciprofloxacin Hydrochloride from Aqueous Solution by Iraqi Porcelinaite Adsorbent. **17**(1): p. 41-49.
21. Bai, S., *et al*., (2014). Effect of polysilicic acid on the precipitation of calcium carbonate. Colloids and Surfaces A: Physicochemical and Engineering Aspects, **445**: p. 54-58.