RESEARCH ARTICLE

Removal of Cationic Dyes (Crystal Violet) by Using Low-cost Surface as an Ecofriendly Surface

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ABSTRACT

This research aimed to study the adsorption properties of the Sodium alginate-g-poly(Acrylic acid-fumaric acid) hydrogel surface on crystal violet dye. Two techniques were used, including [fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM)] to study the surface properties before and after the adsorption process. Several factors such as (equilibrium time, concentration of crystal violet dye, weight of hydrogel, solution of pH, and temperature) were studied. It was found through the results that with increasing the concentration of crystal violet dye, the adsorption efficiency increases, and the removal percentage decreases. On the contrary, by increasing hydrogel's weight, the adsorption efficiency decreases, and the removal percentage increases from (96.12 to 66.33 mg/g), depending on the fullness of the active sites. The removal percentage E% of crystal violet dye using hydrogel surface rise with increased solution pH to reach the maximum pH 6.5 (99.123%). The thermodynamic functions were studied; the reaction was spontaneous and exothermic (ΔH^o (KJ/mol^{-1}) -3.8809). Also, study isotherms and adsorption kinetics were found to fit the Frendlich model (R^2 = 0.9875)and the second-order model (R^2 = 0.849), respectively.

Keywords: Adsorption, Crystal violet, Isotherm, Kinetic, Removal, Thermodynamic.

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INTRODUCTION

It is widely used in textile, paper, coloring, pharmaceutical, cosmetics, plastic, and other industries.[1-4] The dyes are discharged from sewage water, which causes a severe problem due to its high toxicity and accumulation in the environment. Industrial dyes are dangerous pollutants found in water, cause many diseases, and are toxic to humans, microorganisms, and fish species, so removing them from wastewater becomes environmentally important. Large amounts of dyes, hazardous metals, textiles, and paper industries are emitted in sewage, making treatment of polluted water difficult because of the color of these dyes remaining in the water.[5-7] Using several methods, including membrane filtration, photodegradation, adsorption, chemical oxidation, and other methods that remove pollutants from its aqueous solution.[8-10] Adsorption is one of the best techniques used in the removal of pollutants, and that is the use of high-efficiency, inexpensive, and cheap surfaces such as Activated carbon, carbon nanotubes, clay, and other surfaces.[11-13] In this research, it relied on the use of a surface that is easy to prepare from environmentally friendly and inexpensive materials, where the hydrogel is one of the surfaces that have the ability to swelling, and retain pollutants inside, where several important factors were studied, including the effect of dye concentration, weight effect, pH effect, temperature effect, and adsorption isotherms.

EXPERIMENTAL PART

Preparation of Hydrogel

Dissolve 0.25 g of SA in 10 mL of distilled water in a round bottom flask, and the solution was stirred for 1 hour. Then 5 g of AAC and 1 g in 2 mL H2O of solution fumaric acid were added to the above solution, and added 0.05 g in 2 mL H_2O of MBA, stirring the mixture for five minutes after each addition, then passing nitrogen gas for a minute, and then adding KPS in the presence of N_2 gas for a minute, then transferring the mixture to a tube, and placing it in a water bath for two hours.

Preparation of Crystal Violet Dye

The standard solution (1000 mg/L) was prepared by dissolving (1.0 g) in 1000 mL distilled water, A series of solutions were prepared from the standard solution of a dye from (1–25 mg/L) where the calibration curve was determined, and the

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absorbance was measured using UV-vis spectrophotometer, and the calibration curve as appearing in Figure 1.

Adsorption Experiments

Experiments of the Adsorption were carried out in a conical flask (100 mL), where a solution of CV dye (100 mL) by the concentration of CV dye rang 10–100 mg/L solution of dye put in Shaker water bath. The predestine effect of the temperature, the experiments were carried out at three several temperatures, about (10, 20, and 30°C). When added 0.05 g of hydrogel, several pH values (3–10) of the solution of CV dye were adjusted via adding a few drops of (0.1 N HCl or NaOH). The effect of hydrogel weight was studied from (0.005 to 0.125 g). The concentration of a solution of CV dye was estimated by spectrophotometry at a wavelength of 590 nm. The quantity of CV dye adsorbed at equilibrium qe (mg/g), and removal percentage E% ware estimation via the following equation:

$$Qe = \frac{(Co - Ce)v}{M} \quad (1)$$

$$E\% = \frac{Co - Ce)}{Co} \times 100 \quad (2)$$

Co (mg/L) initial concentration of CV dye, Ce (mg/L) equilibrium concentration of CV dye, V (L) volume of the CV dye solution, and m (gm) is the weight of the hydrogel.

RESULTS AND DISCUSSION

Characterization of the Hydrogel Surface

Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared analysis (FTIR) was performed to evaluate the role of functional groups on the hydrogel surface in the adsorption process. Figure 2 shows spectra FTIR of the sample before and after the adsorption process on a CV dye. It was observed from the figure that no new beak appears after the adsorption process, but there is only a small change in the intensity of adsorption and the occurrence of physical adsorption, and it is clear evidence of the success of the adsorption process.[14]

Field Emission Scanning Electron Microscopy (FESEM)

The technique (FESEM) was used to determine the morphological characteristics of the hydrogel surface before and after the adsorption process at the optimum conditions

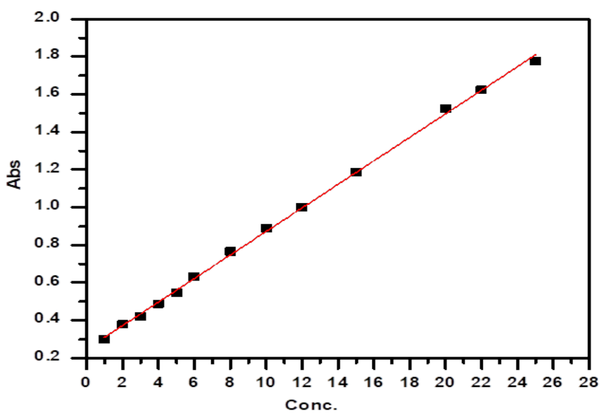

Figure 1: Calibration curve of crystal violet dye.

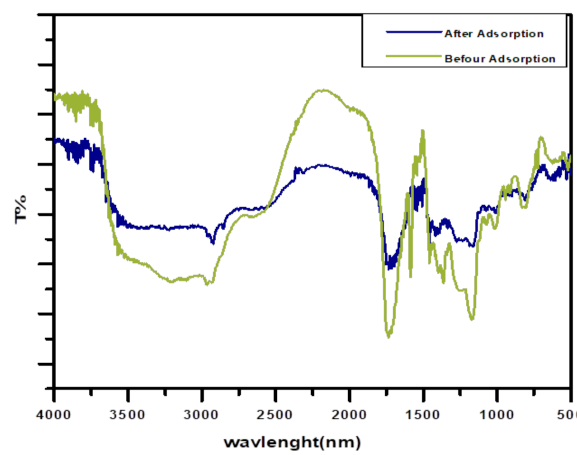

Figure 2: FTIR spectrum of hydrogel before, and after adsorption of CV dye

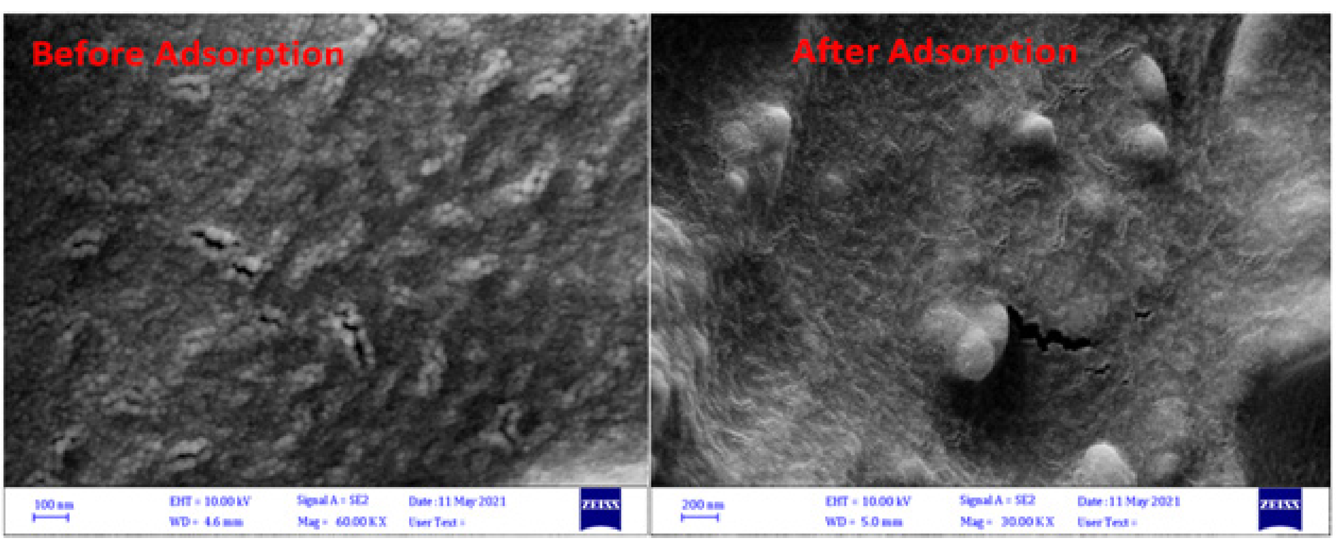

Figure 3: FESEM of hydrogel before, and after adsorption.

of the hydrogel weight and temperature. Through Figure 3, it was found that the surface before the adsorption process contains many active sites, and after the surface adsorption process on a dye, it was noticed that some protrusions appeared on the surface, and the fullness of all the active sites was clear evidence of the research, and success of the adsorption process.[15-17]

Effect of Adsorbent Dosage

The Crystal violet CV uptake data by several quantities (0.005–0.12 g) of the hydrogel as appear in Figure 4. The equilibrium of Crystal violet CV uptake percentage E% increase as the amount of the hydrogel increase because of the increased surface area of hydrogel that gives extra active sites of dye adsorption. The figure also observed that the adsorption efficiency decreases with the increase in the hydrogel surface weight, where the decrease was from (96.12 to 66.33 mg/g), which is clear through the experiment.[18,19]

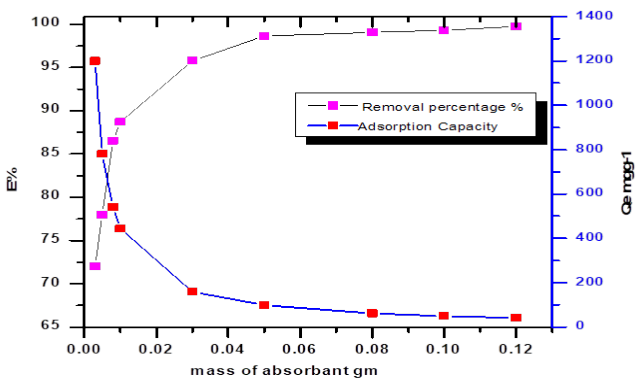

Figure 4: Effect of hydrogel weight on the adsorption efficiency, and removal percentage of CV dye pH 6.5, and Temp 20°C.

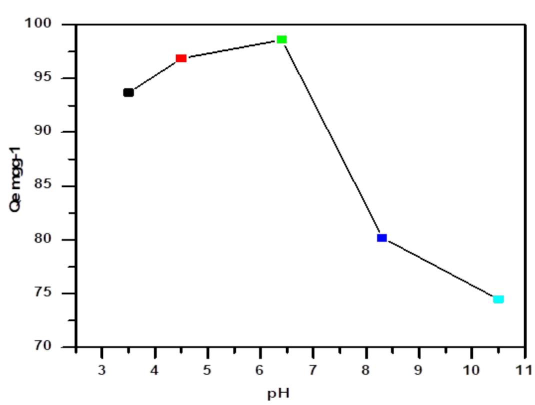

Figure 5: Effect of solution pH on the adsorption capacity onto hydrogel.

Effect of pH

The aqueous solution of the pH is a significant parameter to impact the CV adsorption method by changing the hydrogel charge of an adsorbent and the behavior ionization of dye and adsorbent. The impact pH solution on CV dye removal via the hydrogel as appears in Figure 5. The removal E% of dye CV via surface hydrogel rise with increasing solution pH to reach the best pH 6. 5 after that decrease the solution pH because at lower adsorption efficiency at higher pH could be attributed to the protons rivalry by the dye for the obtainable adsorption sites on the surface hydrogel. Thus, the hydrogel surface might get positively charged when the value of pH 10 is to a definite extent. The electrostatic repulsion among the positive charged hydrogel and CV anion would decrease adsorption efficiency.[20,21]

Effect of Temperature

To determine whether the ongoing adsorption method was exo-thermic or endo-thermic. Isotherms of the adsorption were estimated of several Crystal violet -hydrogel systems. The adsorption capacity of Crystal violet was studied at several temperatures (10 and 30°C) in the presence of different concentrations. Crystal violet dye (10–100 mg.L^{-1}) data are illustrated in Table 1 and appear in Figures 6.

The data appear that adsorption efficiency of the equilibrium of CV dye was rise whereas increasing the temperature solution for whole concentrations CV dye. The adsorbent's efficiency of adsorption changes with temperature. Therefore, the factor of temperature is significant as a physic-chemical method.[13,22]

Study effect of the temperature on adsorption will too help in the calculation of the thermodynamic like Gibbs free energy ΔG), change enthalpy (ΔH), and change entropy (ΔS) of the adsorption method. The adsorption method's equilibrium constant (Ke) at each temperature was calculated from the equations.[10,23]

$$Ke = \frac{(Q_{max}) \times W(g)}{(c_e) \times V(L)} \quad (3)$$

The (ΔG)could be estimated from the equation (4):[24]

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

The of adsorption might be found from equation :

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

When X_m: is the maximum value of adsorption at a certain value of equilibrium concentration (C_e). Plotting $\ln X_m$ vs (1/T)

Table 1: Thermodynamic parameters for CV dye adsorption onto hydrogel.

ΔHo (KJ/mol)	*ΔGo (kJ/mol)*	*ΔSo (J.mol^{-1}.K^{-1})*	*Equilibrium constant*
-3. 8809	-24. 857	28. 226	38. 750
	-21. 305		36. 750
	-20. 255		34. 750

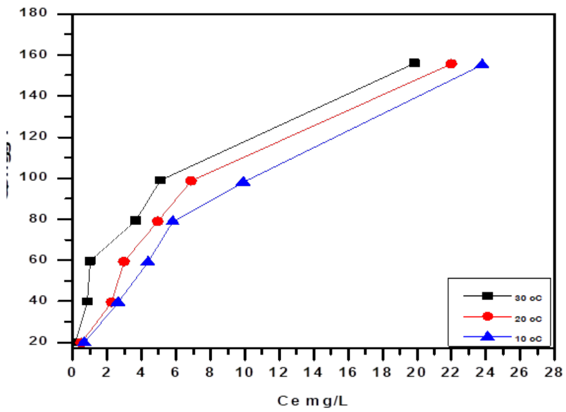

Figure 6: Effect of temperature on the adsorption of CV dye on the hydrogel

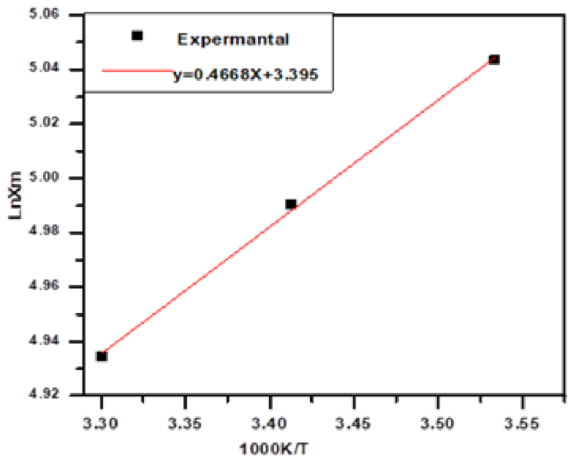

Figure 7: Plot ln Xm against the absolute temperature of the adsorption CV onto hydrogel.

should produce a straight line with a slope -ΔH/R as appear in Figure 7. The value of , and calculated from the intercept, and slope at the same order.[24,25]

Adsorption Model

Langmuir Isotherm

The Langmuir isotherm proposes that mono-layer sorption happens on the surface solid by identical homogeneous sites. It too suggests that no further adsorption takes place once molecules of dye cover the active sites. The saturated mono-layer model is calculated via the equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

Freundlich Isotherm

The Freundlich model is defined through the following equation 7.[26]

$$q_e = K_f C_e^{1/n} \quad (7)$$

The coefficients of estimation (R^2) and model factors from the non-linear regressive process appear in Table 2. A comparison of non-linear curves fitted the experimental result and several models at 10°C, 20°C, and 30°C, as appear in Figures 8.

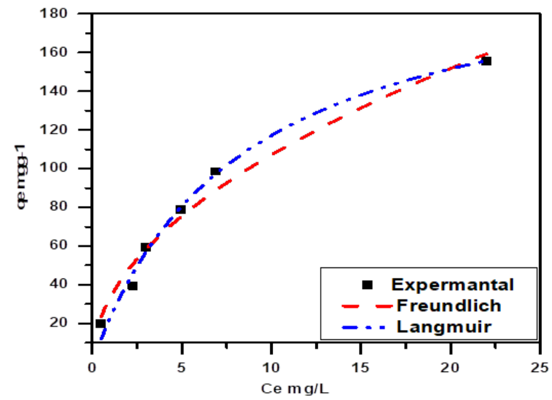

Figure 8: Several absorption model patterns non-linear fit for absorbing the CV dyeonto hydrogel.

Table 2: The Freundlech, Langmuair, the model factors for CV dye absorbed onto hydrogel.

Isotherm models	*Parameters*	*CV*
Langmauir	qm (mg. g^{-1})	214. 813
	KL (L. mg^{-1})	0. 1222
	R^2	0. 9615
Freundlech	KF	33. 582
	1/n	0. 503
	R^2	0. 9875

A plot of q_e versus C_e is shown in Figure (8). Here, K_F and 1/n are obtained from the intercept and slope of the linear regressions (Table 3). The values R2 for the model Langmuir, and model Freundlich at (20°C) are (R2=0.9615), (R2=0.9879) of hydrogel, respectively.[27,28]

Adsorption Kinetics

The kinetics adsorption of CV dye uptake via the hydrogel depends on the equilibrium time of CV, and hydrogel. Different models kinetic using, first-order, second and Elcovich model equation models were analyzed in this study. The first model equation is expressed as follows:

$$q_t=q_e[1-\exp(k_f\, t)] \quad (8)$$

Where *qt* is the amount of adsorbate adsorbed at time *t* (mg.g^{-1}), *qe* is the adsorption capacity in the equilibrium (mg.g^{-1}), k_f is the pseudo-first-order rate constant (min^{-1}), and *t* is the contact time (minutes).

A pseudo-second-order equation based on adsorption equilibrium capacity may be expressed in the form:

$$q_t = -\frac{K_2 q_e t}{1+K_2 q_e t} \quad (9)$$

where K_2 is the pseudo-second-order rate constant (g.gm^{-1}.min^{-1}), the initial sorption rate (expressed in mg.g^{-1}.min^{-1}) can be obtained when t approaches zero, Eq. (10)

$$h = k_2qe^2 \quad (10)$$

The Elkovich equation is used for general application to chemisorption. The equation has been applied satisfactorily

Table 3: Kinetic model first model, second model, and Elcovich model correlation coefficients for CV dye adsorption on the hydrogel.

Model	*Equation*	*Parameters*	*Value*
First model	qt = qe [1-exp (kf t)]	Kt (min^{-1})	0.3108 ± 1.621
		Qe (calc)($mg.g^{-1}$)	93.718 ± 1.822
		R2	0. 298
Second model	qt=	K2 (g/mg/min)	0.3103 ± 0.0410
		Qe (calc)($mg.g^{-1}$) $\frac{1}{\beta}$	98.444 ± 1.322
		R2	0. 849
Elcovich model	qt=1βln(αβ)+	α ($mg.g^{-1}.min^{-1}$)	2.340 ± 1.122
		β ($g.min^{-1}$)	20.951 ± 2.33
		R2	0.7751

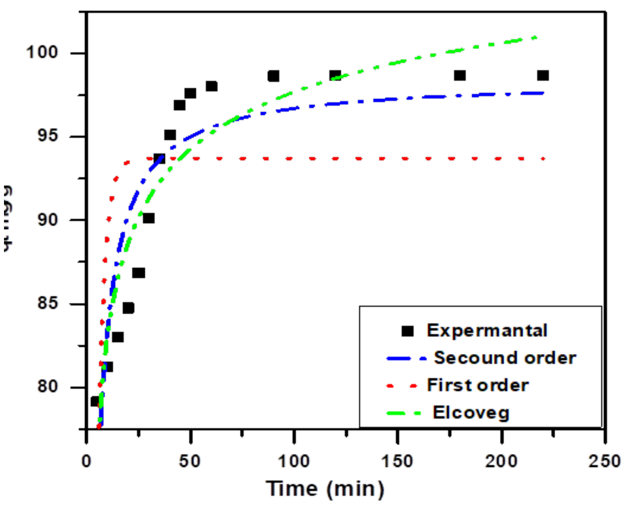

Figure 9: First-order reaction kinetics, second-order, and Elcovich model of CVdye adsorption on hydrogel.

to some chemisorption processes, and has been found to cover a wide range of slow adsorption rates.[29,30] The same equation is often valid for systems in which the adsorbing surface is heterogeneous and is formulated as:

$$qt=\frac{1}{\beta}bln+\frac{1}{\beta}lnt \quad (11)$$

The result of kinetic from the three kinetic models look in Table 3, and Figure 9. The non-linear plots of qt vs t for different primary CV dye concentrations demonstrated good consistency between the experimental and determination values qe. Too, the second-order kinetic model has greater R^2 than the First and Elcovich models. As a result, the adsorption is best suited to the second model than the kinetic of the first, and Elcovich.[8]

CONCLUSION

Hydrogel is a very highly efficient and effective surface that is friendly to the environment and can be prepared from cheaply available materials that can be swelling and retain pollutants inside. Several techniques have been used to determine the properties of the hydrogel surface, including (FTIR, FESEM, TEM). It was found that by increasing the surface weight, the removal parentage% increased, and the best pH at (pH=6.5), which gives the highest adsorption efficiency. The temperature played a key role in knowing the nature of adsorption, as it was observed that with increasing temperature, the efficiency of adsorption increased and that the reaction was spontaneous, as the enthalpy value was negative (-3.8809 (KJ/mol) exothermic, and value of entropy positive (28.226 $J.mol^{-1}.K^{-1}$). Moreover, isotherms of adsorption were also studied, obeying the Kinetic second-order model and Freundlich model.

REFERENCES

1. Gouamid M and Bensaci M B .Adsorption Equilibrium, Kinetics and Thermodynamics of Methylene Blue from Aqueous Solutions using Date Palm Leaves. Energy Procedia. 2013; 36: 898-907.
2. Yazidi A. Adsorption of amoxicilline and tetracycline on activated carbon prepared from durian shell in single and binary systems: Experimental study and modeling analysis. Chemical Engineering Journal. 2020;379: 122320.
3. Bader A T, Zaied A M, Aljeboree A M, Alkaim A F. Removal Of Methyl Violet (Mv) From Aqueous Solutions By Adsorption Using Activated Carbon From Pine Husks (Plant Waste Sources). Plant Archives. 2019;19(2):898-901.
4. Nadher DR, Layth SJ. Synthesis of Graphene Oxide/Hydrogel Composites and Their Ability for Efficient Adsorption of Crystal Violet. J. Pharm. Sci. & Res. 2019;11(2):456-463.
5. Moussavi G, Alahabadi A, Yaghmaeian K, Eskandari M. Preparation, characterization and adsorption potential of the NH4Cl-induced activated carbon for the removal of amoxicillin antibiotic from water. Chemical Engineering Journal. 2020; 217:119-128.
6. Aljeboree AM, Abbas NA, Alkaim AF. Activated Carbon (As A Waste Plant Sources)–Clay Micro/Nanocomposite As Effective Adsorbent: Process Optimization For Ultrasound-Assisted Adsorption Removal Of Amoxicillin Drug. Plant Archives. 2019;19(2):915-919.
7. Abbas NK, Layth SJ. 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. 2019;9(4):558-562.
8. Basam WM, Nadher DR, Layth SJ, Hayder OJ. Synthesis and characterization of polyacrylamide hydrogel for the controlled release of aspirin. J. Pharm. Sci. & Res. 2018; 10(11): 2850-2854.
9. Mhammed A, Atyaa AA, Radhy ND, Jasim LS. A new adsorption material based GO/PVP/AAc composite hydrogel characterization, study kinetic and thermodynamic to removal

Atenolol drug from wast water. IOP Conference Series: Materials Science and Engineering. 2020;928(6):062023.

10. Zaied AM , Ali TB, Aljeboree AM, Alkaim AF. Adsorption And Removal Of Textile Dye (Methylene Blue Mb) From Aqueous Solution By Activated Carbon As A Model (Apricot Stone Source Waste) Of Plant Role In Environmental Enhancement. Plant Archives. 2019;19(2):910-914.
11. Layth SJ, Radhy ND, Hayder OJ. Synthesis and Characterization of Poly (Acryl Amide - Maleic Acid) Hydrogel: Adsorption Kinetics of a Malachite Green from Aqueous Solutions Eurasian Journal of Analytical Chemistry. 2018; 13(1b): em74.
12. Farabi T, SezenKucukcongar M. Removal of methylene blue from aqueous solutions by silica gel supported calix[4]arene cage: Investigation of adsorption properties. European Polymer Journal. 2020;125(15):109540.
13. Aljeboree AM, Alkaim AF. Comparative Removal Of Three Textile Dyes From Aqueous Solutions Byadsorption : As A Model (Corn-Cob Source Waste) Of Plants Role In Environmental Enhancement. Plant Archives. 2019;19(1):1613-1620.
14. Waleed KA, Safaa HG, Nadher DR, Layth SJ. New Approach for Sulfadiazine Toxicity Management using Carboxymethyl Cellulose Grafted Acrylamide Hydrogel. International Journal of Drug Delivery Technology. 2020;10(2):259-264.
15. Safaa HG, Aljeboree MA, Makarim AM, Layth SJ. Synthesis And Characterization Of NTADCIP/P(AA-Co-AM) Composite: Adsorption And Removal Studies Of Drug From Aqueous Solutions Sys Rev Pharm. 2020;11(7):1-6
16. Aljeboree AM. Removal of Vitamin B6 (Pyridoxine) Antibiotics Pharmaceuticals From Aqueous Systems By ZnO. International Journal of Drug Delivery Technology. 2019;9(2):125-129.
17. Aljeboree AM, Alkaim AF. 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. 2019;19(1): 1613-1620.
18. Layth SJ, Aljeboree MA. Removal of Heavy Metals by Using Chitosan/ Poly (Acryl Amide-Acrylic Acid) Hydrogels: Characterization and Kinetic Study. Neuro Quantology. 2021; 19(2): 31-37.
19. Aseel M Aljeboree, Hazim Y Al , Mohammed H S, Alkaim A F . The effect of different parameters on the removal of vitamin B12 drug (as a model biochemical pollutants) by AC/clay. Biochem. Cell. Arch. 2019;19(1):755-759.
20. Saeed UJ, Adnan AK, Saad M, Iftikhar A, Guohua S, Cheng-Meng C, Rashid A. Removal of azo dye from aqueous solution by a low-cost activated carbon prepared from coal: adsorption kinetics, isotherms study, and DFT simulation. Environmental Science and Pollution Research. 2020; 1: https://doi.org/10.1007/s11356-020-11344-4.
21. Aljeboree AM, Alkaim AF. Role Of Plant Wastes As An Ecofriendly For Pollutants (Crystal Violet Dye) Removal From Aqueous Solutions. Plant Archives. 2019;19(2):902-905.
22. Ali MJ, Bassam AJ, Abdulrazzak FH, Alkaim AF, Hussein FH. Synthesis and Characterization of Carbon Nanotubes by Modified Flame Fragments Deposition Method. Asian journal of chemistry. 2017; 29(12): 2804-2808.
23. Kenta S, Suruz M, Kunio O. Low-temperature growth of VO_2 films on transparent ZnO/glass and Al-doped ZnO/glass and their optical transition properties. Thin Solid Films. 2018;651(24): 91-96.
24. Mobasherpour I, Salahi E, Pazouki M. Removal of nickel (II) from aqueous solutions by using nano-crystalline calcium hydroxyapatite. Journal of Saudi Chemical Society. 2011; 15(2):105-112.
25. Jain J, Gupta AK, Bhatnagar VK, Suhas A. Utilization of industrial waste products as adosrbents for the removal of dyes. J. Hazard. Mater. B. 2003;101:31-42.
26. Freundlich HW. The Adsorption of cis- and trans-Azobenzene J Am Chem Soc. 1939;61:2228-2230.
27. Nadavala SK, Anesh MP, Madala S, Mansour I. Equilibrium and Kinetic Studies of Biosorptive Removal of 2,4,6-Trichlorophenol from Aqueous Solutions Using Untreated Agro-Waste Pine Cone Biomass. processes. 2019; 1: 22-33.
28. Alipanahpour ED, Ghaedi AM, Asfaram A, Goudarzi A, Hajati S, Soylak M, Shilpi A, Vinod KG. Modeling of quaternary dyes adsorption onto ZnO-NR-AC artificial 3 neural network: Analysis by derivative spectrophotometry Journal of Industrial and Engineering Chemistry. 2015;1:22.
29. Safa AY, Abdulrazzak FH . Enhance the Growth of Multi- walled Carbon Nanotubes from Coal by Catalytic Chemical Flame Deposition. IOP Conf. Series: Materials Science and Engineering. 2019;571:1-3.
30. Namer AH, Layth SJ. Kinetic Study of removal Zinc Oxide Nanoparticles from Aqueous Solutions on synthesized CH-g-P(AAc-co-Am). IOP Conf. Series: Earth and Environmental Science. 2021;790:012064.