RESEARCH ARTICLE

Removal of Direct Dye from Aqueous Solution by a Low-cost Hydrogel: Adsorption Kinetics, and Isotherms Study

Mohammed A. Jawad,[1] Abed J. Kadhim,[1] Aseel M. Aljeboree[2]*

[1]*Al-Nisour University College, Baghdad, Iraq*
[2]*Department of Chemistry, College of Sciences for Girls, University of Babylon, Hilla, Iraq*

Received: 03rd April, 2021; Revised: 13st July, 2021; Accepted: 09th August, 2021; Available Online: 25th September, 2021

ABSTRACT

This study prepared, characterized, and applied a new surface of Sodium alginate (fumaric acid copolymer polyacrylic acid) hydrogel in removing direct yellow dye from its aqueous solution. Where several modern techniques were used to diagnose the properties of the prepared surface, including [fourier transform infrared spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM)] and one of the most important factors on which the adsorption process depends is pH. The best adsorption was found in the acidic medium, where the adsorption efficiency was (90.112 mg/g). The effect of weight was also studied, and the ideal weight used to obtain the best removal of the DY dye from its aqueous solution (0.05 g) was given, as it gave a removal percentage (93.21%). The adsorption of dye on the hydrogel increased from 140.23 to 155.44 mg/g with increasing temperature from 10 to 30°C, as it was found that the reaction was spontaneous. The equilibrium adsorption result was fitted to isotherm Freundlich and isotherm Langmuir. The best adsorption efficiency from the isotherm Freundlich was estimated to be 155.4 mg/g for the physic-sorption of DY dye on hydrogel. The adsorption was best described via the kinetic second model (R2 = 0.868). The results indicate that hydrogel is a very effective absorbent material in the treatment of pollutants.

Keywords: Direct Dye, Hydrogel, Isotherm, Kinetic, Removal, Thermodynamic.

International Journal of Pharmaceutical Quality Assurance (2021); DOI: 10.25258/ijpqa.12.3.5

How to cite this article: Jawad MA, Kadhim AJ, Aljeboree AM. Removal of Direct Dye from Aqueous Solution by a Low-cost Hydrogel: Adsorption Kinetics, and Isotherms Study. International Journal of Pharmaceutical Quality Assurance. 2021;12(3):191-195.

Source of support: Nil.

Conflict of interest: None

INTRODUCTION

Dyes and organic pollutants have long been identified in water for more than fifty years.[1-3] Its presence in the environment, in general, is related to the disposal of these polluting wastes from factories, hospitals, medical clinics, and textile industries, pharmaceutical industries, and human as well as animal secretions. There are several treatments to get rid of these dangerous pollutants, including chemical treatment, including advanced oxidation processes. However, this process is expensive, so it has relied on Physical treatments, the most important of which is adsorption, one of the most efficient techniques for removing dyes from wastewater. The adsorption process is effective, easy to design, and inexpensive.[4-6] It depends on the use of surfaces with very high efficiency in removing pollutants. It has a high surface area, is inexpensive, and is easy to prepare, such as activated carbon, coconut shells, apricot pods, date kernels, and corn husks.[7-11] Carbon nanotube is one of the most important surfaces in the adsorption process, hydrogel, and clays. In this study, the hydrogel was used. It is considered one of the surfaces with very high efficiency in removing pollutants and is easy to prepare. The surface properties were diagnosed through several techniques FTIR, FESEM, and several factors were studied, including the concentration of the dye and the effect of weight Hydrogel, pH and temperature effect, Kinetic and adsorption isotherms were also studied.

EXPERIMENTAL PART

Preparation of Hydrogel

A total of 0.25 gm is dissolved in 10 mL of distilled water about 0.25 g and left for an hour with continuous stirring, then add from the substance (AAC) about 5 g and 1 g in a solution of fumaric acid 2 mL H_2O to the above solution. After this is 2 mL H_2O (0.05 g MBA), then the solution is left for five minutes with constant stirring after each addition, then KPS is added in the presence of N_2 gas for one minute, then the mixture is transferred to a tube and placed for two hours in a water bath.

Batch Equilibrium Studies

Batch equilibrium studies were carried out utilizing a set of conical flasks of 100 mL by 100 mL of DY dye at several temperatures (10, 20, and 30°C). Primary experiments batch

**Author for Correspondence: annenayad@gmail.com*

were performed at 20°C to study the effects of equilibrium time, pH solution, and hydrogel weight. The optimal conditions that pH of 6.0, equilibrium time of 1 hour, and mass of hydrogel of 0.05 g. The flasks were put in a shaker water bath, and the solutions of DY dye was shaken until contact time, at which the conical was removed, and the solutions were centrifuged at 3000 rpm for 15 minutes, using a UV–Visible spectrophotometer at 450 nm for DY dye.

The quantity of DY dye adsorbed at equilibrium Qe (mg/g) and percentage removal E% ware calculated by the following equation:

$$Qe = \frac{(Co - Ce)V}{W} \quad (1)$$

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

Here, Co (mg/L) primary conc. of DY dye, Ce (mg/L) concentration of DYdye at equilibrium, V (L) volume solution of the DY dye, and W(g) is the mass of hydrogel.

RESULTS AND DISCUSSION

Characterization of the Hydrogel Surface

The spectrum of FTIR appears in Figure 1. The bands range at about 1700 cm^{-1} due to the shift in the stretching vibration connected with the hydrogen directly overtone for bonded labor absorption strong C=O group. The sharp peak at 1650 cm^{-1} duo to the C=O group and associated with the amide group. Due to the N-H and O-H bands, a much broader absorption peak in 3100 and 3450 cm^{-1} is associated with polymer chains.[19,20] The wide peak at 3450 cm^{-1} is duo to a representative peak of the primary amine. The weak peak at 1550 cm^{-1} is attributed to O-H band in the –COOH group. The bands at 1720–1700 cm^{-1} duo to a characteristic are carbonyl groups in the carboxylic acids. The weak peaks at 1020 and 1200 cm^{-1} duo to C-N bands and the weak peaks at 2800 and 1410 cm^{-1} are attributed to -CH_2- groups on the polymer chains.[12,13]

FESEM

In Figure 2, the technique FESEM was used to determine the hydrogel surface properties before and after the adsorption process, where it was noticed that the surface is smooth before the adsorption process. However, after loading the dye, the surface of the hydrogel became rougher, and the appearance of irregular agglomerations is clear evidence of the dye loading on the surface of the hydrogel.[14,15]

Effect of Weight of Hydrogel

The solid/solution ratio is a significant issue estimation the efficiency of a mass of hydrogel in batch sorption was evaluated. The influence of the weight of hydrogel on the removal percentage E% of direct yellow appears in Figure 3. It obeys the predicted style of rising percentage dosage as the weight was increased. This is possible because of the resistance to mass transfer of natural yellow from liquid bulk to the solid surface, Which becomes significant at great loading adsorbent in conducted experience. The percentage removal of Direct yellow increased through rising the quantity of hydrogel. However, the quantities of the hydrogel's direct yellow per unit mass (Qe) decreased by increasing the solid/solution ratio (Figure 3). The E% of the direct yellow raised when the mass

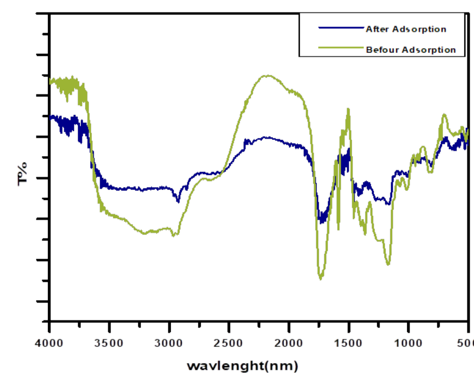

Figure 1: FTIR spectrum of hydrogel before, and after adsorption of DY dye.

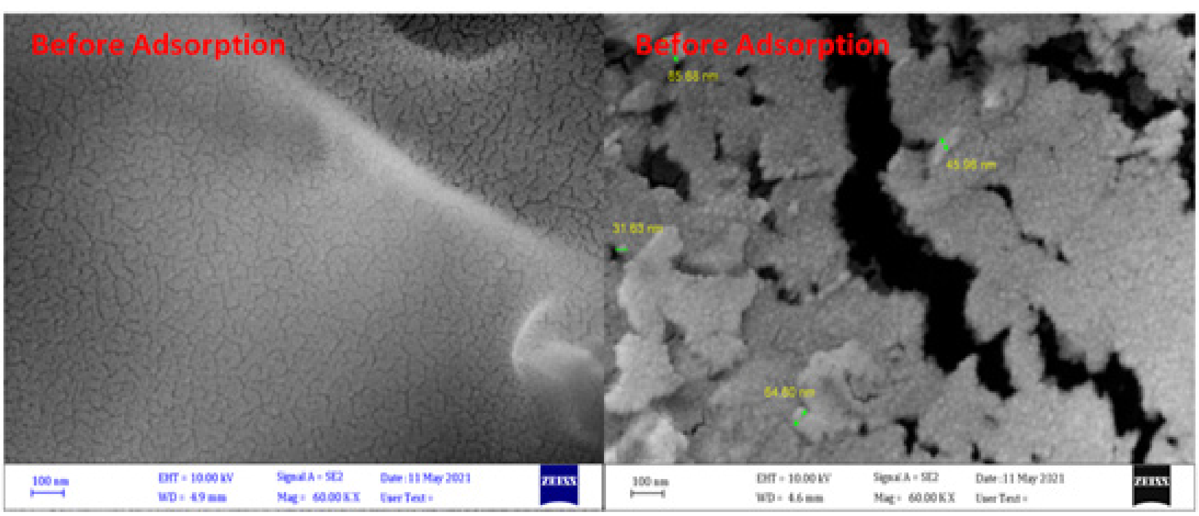

Figure 2: FESEM image of hydrogel surface before and after adsorption

of hydrogel was altered (0.005 to 0.12) g at concentrations of direct yellow (100 mg/L).[16,17]

Effect pH Solution on Direct Yellow Adsorption

The pH solution of the direct yellow plays a significant part in the complete adsorption method and particularly in the adsorption efficiency. The effect pH solution range (3–10) on the equilibrium uptake efficiency of direct dye yellow was studied at direct yellow concentrations (100 mg/L) at 20°C. As shown in Figure 4, the direct yellow uptake decreased by an increased pH solution. As the solution pH of the adsorption is lower, increase the positive charges on to hydrogel surface. As the solution pH of the adsorption is lower, thus increase the positive charges on to hydrogel surface. This would pull the functional groups of negatively charged located on the direct yellow dye.[18,19]

Effect of Temperature Solution

In order to look at the impact solution of temperature, the adsorption studies were carried out for the concentration of direct yellow dye at 100 mg/L at three several temperatures, about 10, 20, and 30°C, at pH 6.5, as appear in Figure 5. The adsorption efficiency versus the equilibrium of concentration of direct yellow dye at several temperatures. It was observed that the adsorption capacity of dye increase from 140.23 to 152.54 mg/g with the temperature increase from 10 to 30°C, indicating the nature exothermic of the adsorption study the adsorption thermodynamics of direct yellow dye onto hydrogel, three parameters basic of the thermodynamic, enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG), to estimation by using equations:[20]

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

$$K_e = \frac{(Q_{max}) \times Wt}{(C_e) \times v} \quad (4)$$

T/temperature solution (K), Ka equilibrium constant of the adsorption, and R is the gas constant. Entropy and Enthalpy were calculated from intercept and slope from qe vs. 1/T (Figure 6).

The data appear in Table 1. The value negative of enthalpy (21.0701 kJ.mol^{-1}) indicates that the adsorption of direct yellow dye onto hydrogel the process exothermic. The (ΔG) values are negative when increase temperature from 20–30°C, The adsorption of direct yellow dye onto hydrogel is spontaneous and favorable of thermodynamically. Gibbs free energy rises about -21.6544 to -20.255 kJ.mol^{-1}, When increase temperature

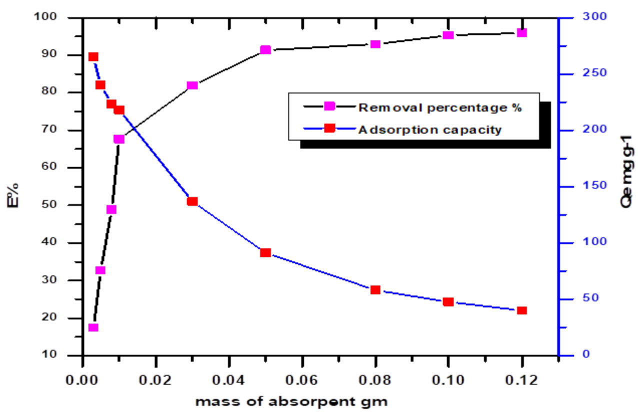

Figure 3: Effect of the weight of hydrogel on the adsorption efficiency and percentage removal of direct yellow DY dye pH 6.8 and Temp 20°C.

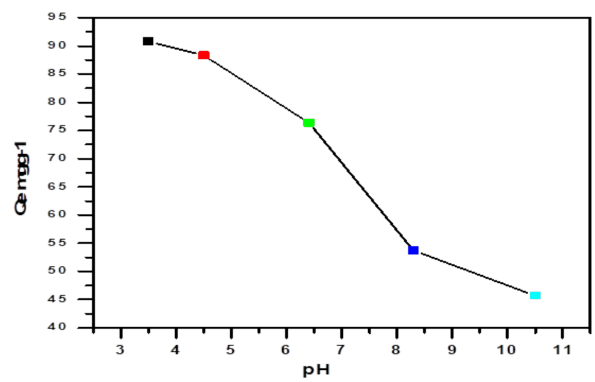

Figure 4: Effect of solution pH on the adsorption capacity onto hydrogel.

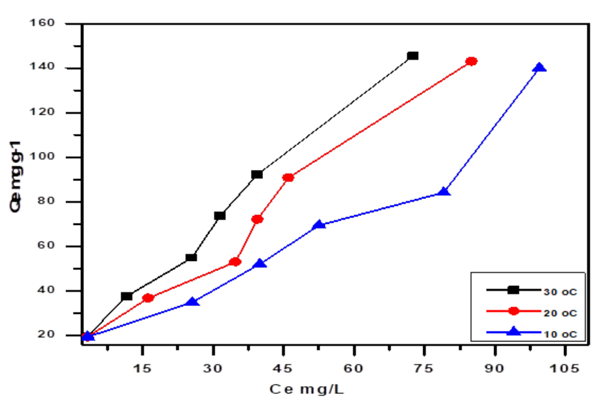

Figure 5: Effect of temperature on the adsorption of DY dye on the hydrogel

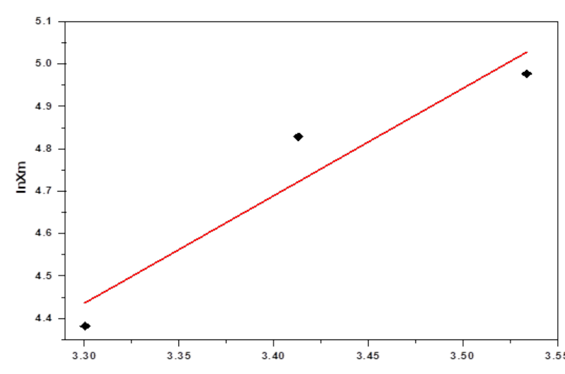

Figure 6: Plot ln Xm against the absolute temperature of the adsorption DY onto hydrogel.

from 20–30°C. The value negative ΔS (32.649 $J.mol^{-1}.K^{-1}$) indicates a decrease in the degree of freedom of adsorption direct yellow dye onto hydrogel.[21]

Adsorption Model

The capacities of hydrogel to adsorb direct yellow was studied via measuring the concentrations of direct yellow at pH 6.5 and 20°C in batch systems. Freundlich isotherms model and Langmuir isotherm model were utilized to normalize the adsorption result.[22] The data appear that the isotherm Freundlich model close-fitting best (R2 = 0.9688) and isotherm Langmuir (R2 = 0.9508) demonstrating that the adsorption of direct yellow dye on to hydrogel can be considered to be a mono layer adsorption method.[23] The isotherm Freundlich equation was utilized to refer to the relationship among the quantity of direct yellow adsorbed and its equilibrium concentration in solutions (Figure 7) calculated factors from Isotherm Langmuir and isotherm Freundlich tof the equation adsorption model as appear in Table 2.

Adsorption Kinetics

The kinetic model of the adsorption result was analyzed utilizing the first model, second model, and Elcovich model.

Table 1: Thermodynamic parameters for direct yellow dye adsorption on to hydrogel

ΔH° (KJ/mol)	*ΔG° (kJ/mol)*	*ΔS° (J.mol⁻¹.K⁻¹)*	*Equilibrium constant*
	-21.6544		9.931
-21.0701	-21.3052	32.649	8.561
	-20.255		5.479

Table 2: Different parameters isotherm models for the adsorption study of DY dye onto hydrogel

Temperature/ °C		20°C
Freundlich	KF	31.244 ± 1.3319
	1/n	0.858 ± 0.1042
	R^2	0.9688
Langmuir	qm (mg/g)	843.97 ± 86.44
	KL (L/mg)	0.024 ± 0.0022
	R^2	0.9508

The Lagargren -first model is represented via the equation:

$$1\ q_t=q_e[1-\exp(k_f t)] \quad (5)$$

kinetic model of the c second-order can be expressed as follows:

$$q_t \frac{K_2 q_e t}{1+K_2 q_e t} \quad (6)$$

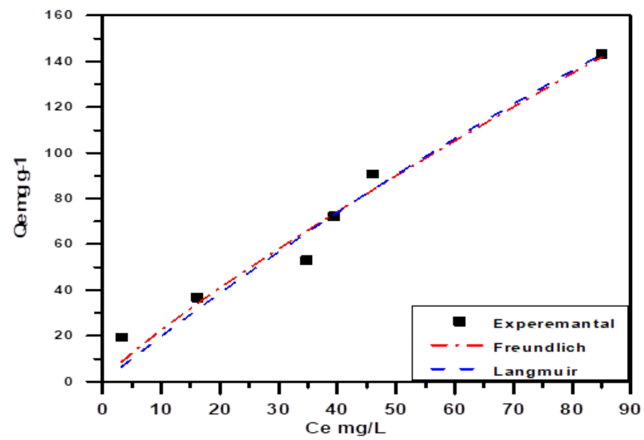

Figure 7: Different absorption isotherm patterns non-linear fit for absorbing the DY dye on to hydrogel,

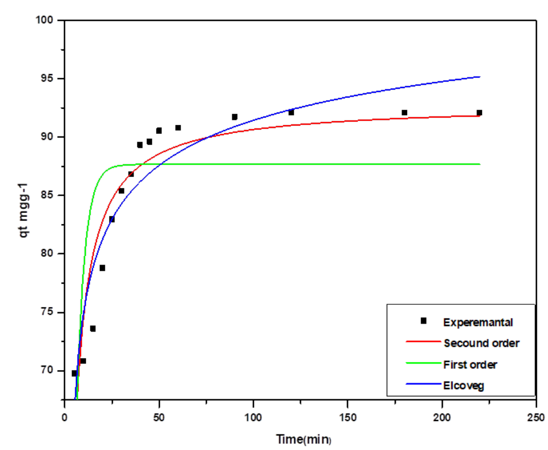

Figure 8: Kinetics model of first-order, second order, and Elcovich model of DY dye adsorption on hydrogel.

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

Model	*Equation*	*Parameters*	*Value*
First model	qt = qe [1-exp (kf t)]	Kt (min^{-1})	0.230 ± 0.032
		qe (calc) ($mg.g^{-1}$)	87.676 ± 1.722
		R2	0.4334
Second model	qt = K2qe2t/(1+K2qet)	K2 (g/mg/min)	0.414 ± 0.0616
		qe (calc) ($mg.g^{-1}$)	92.84 ± 1.324
		R2	0.868
Elcovich model	qt = 1/β[1βln(αβ)]+ 1/β(lnt)	α ($mg.g^{-1}\ min^{-1}$)	10.37 ± 3.211
		β ($g.min^{-1}$)	32.644 ± 2.422
		R2	0.8322

The equation Elkovich model is utilized for general application to chemi-sorption. The same equation is often valid for systems in which the adsorbing surface is heterogeneous and is formulated as:

$$qt = \frac{1}{\beta} 1\beta \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (7)$$

The kinetics of the adsorption method, which defines the investigational result, elected for adsorption of direct yellow dye onto hydrogel as appear in Figure 8. Experimental result study was done utilizing the first, second, and Elcovich model Table 3 data display adsorption of direct yellow dye via the hydrogel is an achievable process because (R2) value is best of second model compared to the first and Elcovich model.[15,24,25]

CONCLUSION

In this study, the effect of temperature had an important and very effective role in removing the direct yellow dye from its aqueous solutions using an effective, cheap, inexpensive and environmentally friendly hydrogel surface. It was noticed that the temperature increased, the adsorption efficiency increased as it gave the best removal of the dye at the high temperature. The adsorption isotherms were also studied and were obeying Friendlich model. Three types of Kinetic models were studied, where the best model was the second-order model.

REFERENCES

1. Hameed KS, Muthirulan P, Meenakshi SM, Adsorption of chromotrope dye onto activated carbons obtained from the seeds of various plants: Equilibrium and kinetics studies. Arabian J. Chem, 2017;10:S2225-S2233.
2. Layth, SJ and Aljeboree MA, Removal of Heavy Metals by Using Chitosan/ Poly (Acryl Amide-Acrylic Acid)Hydrogels: Characterization and Kinetic Study. NeuroQuantology, 2021;19(2):31-37.
3. Aseel M Aljeboree, ANA, Colorimetric determination of Amoxicillin using 4-Aminoantipyrine and the effects of different parameters. Journal of Physics: Conference Series, 2019:12(5): 52-67.
4. Mahdi, A.B., Aljeboree, A.M., Alkaim, A.F., Adsorption and removal of pollutants (Dyes) from wastewater using different types of low-cost adsorbents: A review. Journal of Chemical Health Risks, 2021;11(2):203-212.
5. Santos, SCR. and RAR Boaventura, Adsorption of cationic and anionic azo dyes on sepiolite clay: equilibrium and kinetic studies in batch mode. J. Environ. Chem. Eng., 2016;4:1473-1483.
6. Aljeboree, A.M., Removal of Vitamin B6 (Pyridoxine) Antibiotics Pharmaceuticals From Aqueous Systems By ZnO. International Journal of Drug Delivery Technology 2019;9(2): 125-129.
7. Aljeboree AM, Adsorption and removal of pharmaceutical riboflavin (RF) by rice husks activated carbon. International Journal of Pharmaceutical Research 2019;11(2):255-261.
8. Thitame PV, and SR Shukla, Adsorptive removal of reactive dyes from aqueous solution using activated carbon synthesized from waste biomass materials. Int. J. Environ. Sci. Technol., 2016;13: 561-570.
9. Gamoudi, S. and E. Srasra, Adsorption of organic dyes by HDPy+-modified clay: effect of molecular structure on the adsorption. Journal of Molecular Structure, 2019.
10. Mahde BW, Radia ND, Jasim LS, Jamel HO. Synthesis and characterization of polyacrylamide hydrogel for the controlled release of aspirin. Journal of Pharmaceutical Sciences and Research. 2018 Nov 1;10(11):2850-2854.
11. Aseel M. Aljeboree, A.F.A., Ali loay, hanadi m algburi, Photocatalytic Degradation of Textile Dye Cristal Violet Wastewater using Zinc Oxide as a Model of Pharmaceutical Threat Reductions. Journal of Global Pharma Technology, 2019;11(2):138-143.
12. Tian W, Deng Ze Wang, Hongyan, Liu, Honglin, Li, Guizhong, Liu, Xuejun, Chen, Zhenhong, Chen, Hao,Li, Yanan, Negative adsorption in the isotherm adsorption experiments of low-adsorption coal and shale. Natural Gas Industry B, 2019; 6(1):44-50.
13. Liu, M., et al., Adsorption of methyl blue from solution using walnut shell and reuse in a secondary adsorption for Congo red. Bioresource Technology Reports, 2019;5:238-242.
14. Nadher, D.R., Layth S J., Synthesis of Graphene Oxide/Hydrogel Composites and Their Ability for Efficient Adsorption of Crystal Violet. J. Pharm. Sci. & Res., 2019;11(2):456-463.
15. Ayad F. Alkaim, AMA, White Marble as an Alternative Surface for Removal of Toxic Dyes (Methylene Blue) from Aqueous Solutions International Journal of Advanced Science and Technology 2020;29(5):5470-5479.
16. Aseel M. Aljeboree, A.N.A., Ayad F. Alkaim, Highly Efficient Removal of Textile Dye "Direct Yellow (Dy12) Dyes" From Aqueous Systems Using Coconut Shell as a Waste Plants. Plant Archives 2020;20(1):3029-3038.
17. Hussain NA, Jasim LS. 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: p. 012064.
18. Ali T. Bader, Z.-A.-m., Aseel M. Aljeboree, Ayad F. Alkaim, 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.
19. Powers, H.J., Riboflavin (vitamin B-2) and health. Am. J. Clin. Nutr., 2003;77(6):1352-1360.
20. Konicki W, Sibera D, Mijowska E, Lendzion-Bieluń Z, Narkiewicz U. Equilibrium and kinetic studies on acid dye Acid Red 88 adsorption by magnetic $ZnFe_2O_4$ spinel ferrite nanoparticles. Journal of Colloid and Interface Science, 2013;398:152-160.
21. Farhan AM, Al-Dujaili AH, Awwad AM. Equilibrium and kinetic studies of cadmium (II) and lead (II) ions biosorption onto Ficus carcia leaves. International Journal of Industrial Chemistry. 2013 Dec;4(1):24.
22. Aljeboree AM, Mahdi MA, Jasim LS. Synthesis And Characterization Of NTADCIP/P (AA-Co-AM) Composite: Adsorption And Removal Studies Of Drug From Aqueous Solutions. Systematic Reviews in Pharmacy. 2021;12(1):282-289.
23. Alkaim AF, Aljobree AM, Alkaim AF. Adsorption and photocatalytic degradation of pharmaceutical amoxicillin using TiO2 nanoparticles in aqueous solutions: oxidative coupling as spectrophotometric method international journal of advanced. Sci. Technol.. 2020;29(5):5480-5487.
24. Ghaedi M, Sadeghian B, Pebdani AA, Sahraei R, Daneshfar A, Duran C, Kinetics, thermodynamics and equilibrium evaluation of direct yellow 12 removal by adsorption onto silver nanoparticles loaded activated carbon. Chem. Eng. J., 2012. 187: p. 133-141.
25. Yao, Y., Bing, H., Feifei, X., Xiaofeng, C., Equilibrium and kinetic studies of methyl orange adsorption on multiwalled carbon nanotubes. Chem. Eng. J., 2011. 170(1): p. 82-89.