RESEARCH ARTICLE

Removal of Amoxicillin Drug from Aqueous Solution by using Marble Powder Surface Activated by Several Acids

Majeed M Abid[1], Zainab AA Alhassan[2], Saad K Mohammed[3], Mahdi K Ali[4], Alaa A Omran[5*]

[1]*Department of Pharmacy, Al Hadi University College, Baghdad, Iraq.*
[2]*Department of Pharmacy, Mazaya University College, Iraq.*
[3]*Al-Manara College for Medical Sciences, Maysan, Iraq.*
[4]*National University of Science and Technology, Dhi Qar, Iraq.*
[5]*Department of Medical Engineering, AL-Nisour University College, Baghdad, Iraq.*

Received: 19th July, 2023; Revised: 18th September, 2023; Accepted: 07th October, 2023; Available Online: 25th December, 2023

ABSTRACT

In recent years, the problem of the removal drug from wastewater has become one of the most important global problems due to the accumulation of large quantities of drugs on the surface of the water, which causes a lack of penetration of sunlight into water contaminated with drug, and this leads to a reduction in aquatic life forms for all living organisms and also leads to problems large environmental impacts and many dangerous diseases for humans. An attempt was made to prepare an environmentally friendly, economical and available surface that has a high absorption capacity to remove the contaminants of pharmaceuticals such as amoxicillin (AMX) drug. In this study, waste material such as white marble was used as an absorbent material, and its adsorption properties were enhanced and activated by treating it with several acids (HCL, H_2SO_4, and HNO_3). The prepared white marble before and after adsorption were characterized by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The influence of several parameters like contact time (5–120 minutes), initial concentration of drug (10–50 mg/L), adsorbent dosage (0.02–0.2 g), solution temperature (10–40°C), and pH (2–10) was estimated for adsorption method optimization. The equilibrium adsorption result was examined utilizing the isotherm Langmuir, and isotherm Freundlich models. The attained data indicated that, sorption was found to be fast, 84.44% within 1 hour.

Keywords: Removal, White marble, Isotherm model, Drug, Pharmaceutical, Adsorption.

International Journal of Drug Delivery Technology (2023); DOI: 10.25258/ijddt.13.4.14

How to cite this article: Abid MM, Alhassan ZAA, Mohammed SK, Ali MK, Omran AA. Removal of Amoxicillin Drug from Aqueous Solution by using Marble Powder Surface Activated by Several Acids. International Journal of Drug Delivery Technology. 2023;13(4):1204-1208.

Source of support: Nil.

Conflict of interest: None

INTRODUCTION

At present, wastewater contaminated with dyes is mainly obtained from textile industries such as clothing, paper, leather, cosmetics, rubber, food, plastic and pharmaceutical industries. Because this polluted water resulting from industries is discharged into clean water in large quantities, this leads to the formation of highly toxic complexes in very large quantities that are difficult to remove and cause danger to living organisms and also cause environmental pollution. Present treatment ways for pollutants contain chemical, physical, and biological ways, and so on. Several removal methods have been studied *via* adsorption, photocatalytic degradation, oxidation, biological treatments, liquid membrane separation, chemical coagulation, and electrolysis.[1-4]

Adsorption studies are usually focused on adsorbent selection, and articles, which estimate its performance for pollutant removal can be generally created on the literature: Agro-industrial by-products, activated carbon, chitosan, industrial waste, limestone, refuse concrete, marble, granite, refuse cement, shell, mineral zeolite, minerals, bacterial and fungal biomass, amid others has already been considered. The studies involving this material presented that it could be a more efficient and low-cost material for drug uptake.[5-12]

Marble waste is preferred over other absorbent materials in the treatment and removal of wastewater due to its very high effectiveness in removing pollutants and it is also available, cheap and inexpensive. Studies have shown that marble waste is considered a good absorbent material for removing pharmaceutical preparations.[13,14] One of its distinctive characteristics is its cost and availability in the environment compared to activated carbon. Marble is a type of metamorphic rock created from limestone, which results from the exposure of rocks to high pressure and heat in the ground. Limestone, known as marble, is a type of sedimentary rock that consists

**Author for Correspondence: aishamohaisha7@gmail.com*

of animal skeletons and marine corals from the sea. Marble or limestone is composed of the mineral calcite. The crystals of calcite dissolve and crystallize several times to become coarser and larger crystals that intertwine, and then the carbonate rock known as limestone (marble) forms a shiny, clean, pollution-free marble.[15,16]

AMX is one of the types of antibiotics that belong to the amino penicillin group, which is classified as a penicillin group as shown in Figure 1. Amoxicillin has important therapeutic uses, including the treatment of bacterial infections, skin infections, urinary tract infections, pneumonia, strep throat, dental infections, and middle ear infections. In general, the medication is taken orally.[17-20] In this study, use a surface from white marble waste, which is environmentally friendly, available and advantage of highly efficient in removing of AMX drug from an aqueous solution. Several factors affecting the adsorption process were studied, such as the effect of equilibrium time, the effect of drug concentration, the effect of the weight of the adsorbent, and the effect of temperature. Two types of adsorption isotherms were also studied, and the results obeyed the Freundlich isotherm.

MATERIALS AND METHODS

Preparation of White Marble Powder

The white marble utilized in this research was purchased in the form of stone from the local market in Hilla, Iraq. The stone of white marble as a waste was ground to obtain fine powder to be utilized as an adsorbent to remove AMX drug. After a process of preparing the white marble powder, it is divided into three parts, each part contains 10 g from powder. The first part is activated and treated with a solution of (0.1 N HCl), the second part solution of (0.1N H_2SO_4) and the third part (0.1N HNO_3). Leave with continuous stirring for a period of (24 hours) at room temperature. After that, washed with distilled water to remove all water-soluble impurities, then dried in oven at 150°C for 6 hours. The samples were ground and sieved to obtain a fine powder. It was kept in glass bottles and used in all experiments.

Optimization of Adsorption Parameters

The effect of the initial concentration AMX drug , adsorption dose, temperature, solution pH and equilibrium time via changing concentration drug from 10–50 mg/L and adsorption dose of white marble from (0.02–0.2 g), pH solution from (2–10) , solution of temperature from (10–40°C) were investigated. The equilibrium time was 60 minutes for 350 rpm to remove the adsorbent and were measured at a wavelength for maximum absorbance (λ_{max} is 272 nm for AMX drug).

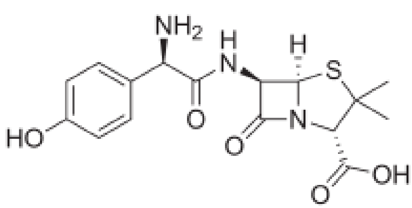

Figure 1: Chemical stretcher of amoxicillin AMX drug

RESULTS AND DISCUSSION

Characterization

Figure 2 (a and b) shows image field emission scanning electron microscopy (FESEM) of white marble before and after the adsorption process. The FE-SEM images (a) show surface asymmetry and also have a rock-like morphology. It agglomerates on a surface and was also found to contain small aggregates growing on rocks, mainly due to the components present. On the surface of white marble. And FE- SEM micrograph of white marble after the adsorption process in Figure 2 b indicated that the surface became spherical and uneven with random aggregates with an increase in surface porosity.[21,22] Many pores were well developed in white marble and this results in white marble with a high and good porosity structure that is suitable for the adsorption process successfully. The morphology of the prepared surface was analyzed using transmission electron microscopy (TEM) analysis (50 nm), as shown in Figure 2 c. It was evident that a more agglomerated black cloud formed on the surface and the formation of a new geometry, which was attributed to the process of treating the surface with acid, where the presence of agglomerations and the formation of dark colors were observed.[23]

Effect of contact time

The drug solution (30 mg.L^{-1}) is prepared and placed in conical flask 100 mL with a weight of white marble (0.15 g/100 mL) in a water bath shaker at 25. Use a spectrophotometer to evaluate the concentration of the AMX drug, at the equivalent wavelength of maximum, centrifugation is used to isolate samples at different time intervals Figures 3.

The influence of equilibrium time was studied with the of 30 mg/L AMX drug concentrations at 25°C. The adsorption efficiency as a function of equilibrium time and concentration of drug. The adsorption rises quickly at the primary 10 minutes; the uptake rate is originally fast until an equilibrium value

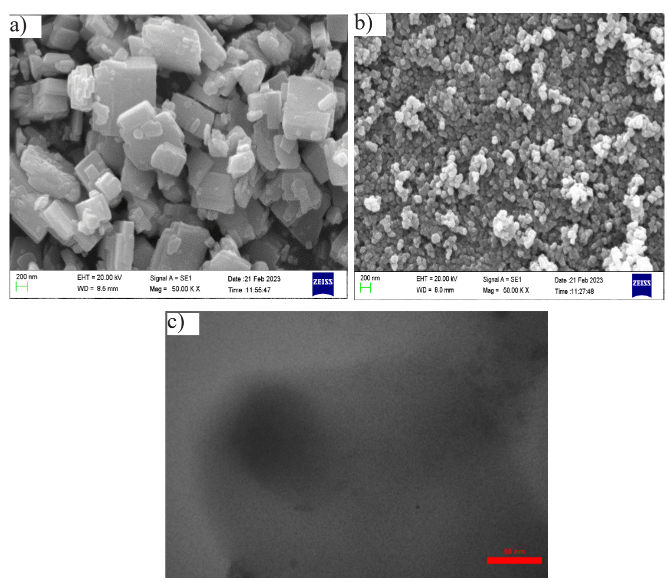

Figure 2: Image FE-SEM a) White marble before and b) after the adsorption process and c) TEM of white marble.

is reached next 60 minutes of contact. When 30 mg/L of concentration AMX drug was raised at 25°C, the adsorption efficiency raised from (9.55–16.67 mg/g), while the percentage removal increased from (49.72–84.26%).[24,25]

Effect weight of white marble

The impact of the weight of white marble was required to observe the smallest probable quantity, which illustrates the best adsorption capacity. The weight of white marble was different from (0.02–0.2 g) . The data appear in Figure 4.

The influence of the dosage white marble on the removal of E% AMX drug adsorbed from an aqueous medium presented that raising the dosage white marble steadily enhanced the elimination of AMX., increasing the mass t of white marble from 0.02 to 0.2 g are followed by raising the removal E% from 40.639 to 98.085%. Increasing the weight of white marble results in a decrease adsorption efficiency of AMX from 16.39 to 40.08 mg/g.[4,18,26] Further increasing in the amount of white marble used from 0.08 - 0.1 g had no influence on E% of AMX removed.[18,27,28]

Effect of solution pH

The effect of solution pH is one of the most important factors that must be studied when analyzing adsorption behavior with adsorbent materials. According to the results shown in Figure 5. presents the influence of solution pH from (2–10) onto adsorption efficiency AMX on white marble. At the best optimum conditions (25°C, 30 mg/L and 100 mL) AMX adsorbed on 0.15 g white marble, 1-hour equilibrium time. The adsorption capacity for AMX was maximum at pH 10 (19.306 mg/g) , lowest adsorption was reached at pH 2 (7.46 mg/g). Also, the removal percentage% decreased with increased pH solution and the best E% at pH 10 (99.11%) , lowest adsorption was reached at pH 3 (37.44%).[22,29]

Effect of solution temperature

Temperature is considered an important influence on the adsorbate and adsorbent in order to get rid of contaminants, as an adsorption study was conducted for a concentration of 30 mg/L AMX drug at different temperatures of 10, 20,30 and 40°C, at a pH of 6. As shown in Figure 6, the adsorption efficiency versus different temperatures. It was observed that the adsorption of removal percentage of AMX drug increases from 33.43 to 90.45% as the solution temperature increases from 10 to 40°C, which indicates an endothermic reaction.[30-32]

Adsorption isotherm

Analyzing the equilibrium isotherm result of the adsorption model by fitting into two models is an important step to find the appropriate isotherm that can be used for design purposes. In this work, two adsorption models, Langmuir isotherm and Freundlich isotherm, in their nonlinear forms, were applied to the equilibrium data of AMX drug adsorption by white marble. The values of the isotherm constants are the correlation coefficients R2 given in Table 1 and Figure 7. The calculated R2 values proposed for the Langmuir isotherm and Freundlich isotherm models fit well with the result on the adsorption equilibrium of the AMX drug. The best (qmax) according to the Langmuir isotherm model was found to be 80 mg/g at 25°C.[33]

The isotherm Langmuir assumes uniform energies of sorption onto the surface and no transmigration of sorbate in the plane of the surface.[34] The equation linear of isotherm Langmuir model in equation (1)

$$\frac{C_e}{q_e} = \frac{1}{q_m \cdot K_L} + \left(\frac{1}{q_m}\right) * C_e \quad (1)$$

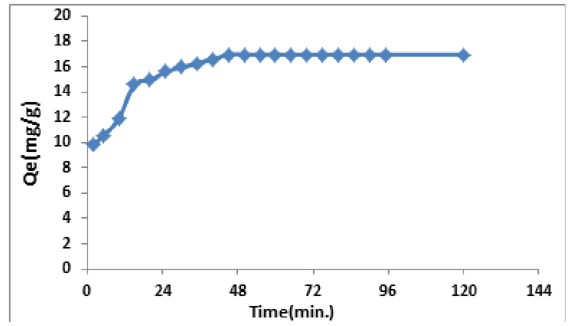

Figure 3: Effect of equilibrium time onto removal of AMX drug

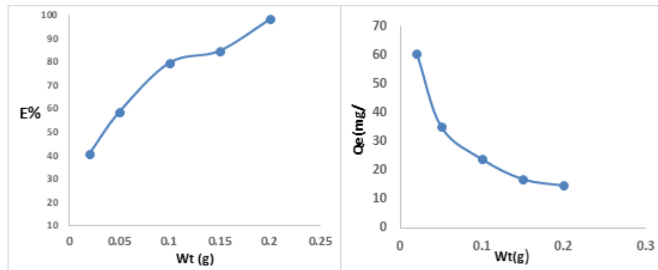

Figure 4: Effect of weight of white marble on to removal AMX drug

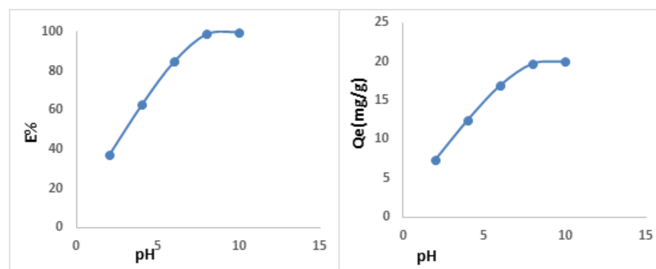

Figure 5: Effect of solution pH on white marble on the removal AMX drug

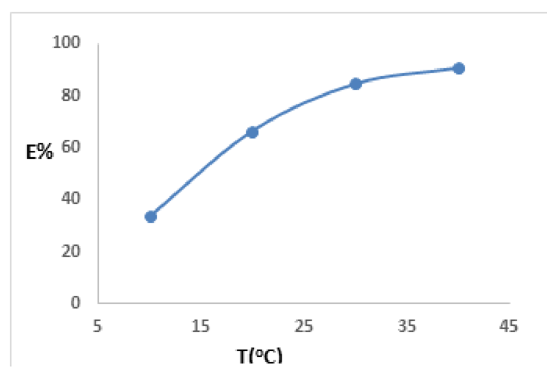

Figure 6: Effect of solution temperature on white marble on the removal AMX drug

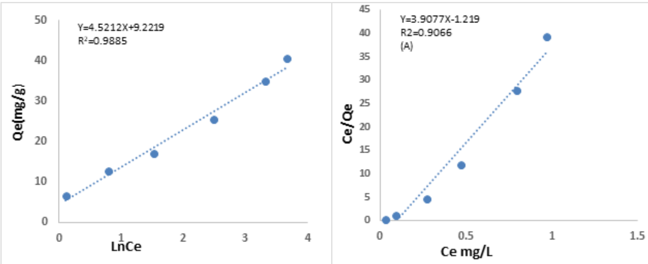

Figure 7: Two adsorption isotherm linear A) Langmuir, B) Freundlich fit of adsorption AMX drug on white marble

Table1: Two adsorption isotherm linear fit of adsorption AMX drug on white marble

Isotherm models	*Factors*	*white marble*
	K_F	86.765
Freundlich	1/n	0.232
	R^2	0.9885
	q_m (mg/g)	80.12
Langmuir	K_L(L/mg)	0.123
	R^2	0.9066

Table 2: Activated and treatment of white marble surface

Type of acid	*Adsorption capacity (Qe mg/g)*
HCl	17.87
H_2SO_4	12.22
HNO_3	10.12

In Freundlich isotherms, the value of n (0.232) indicated favorable adsorption of AMX drug onto white marble via physicochemical adsorption on the heterogeneous surface of the white marble. It has been suggested that a value of n between 1 and 10 represents a useful absorption mode. The calculated KF value in Freundlich isotherms was 86.54 indicating efficient adsorption of AMX drug via white marble.[30, 35] Freundlich isotherm is an empirical equation based on adsorption onto surface hetero-geneous. The equation linear of isotherm Freundlich model in equation (2)

$$\ln q_e = \ln K_f + \frac{1}{2} C_e \qquad (2)$$

Activated and treatment of white marble surface

The white marble surface was activated using three acids (HCl, HNO_3,and H_2SO_4), and from the results shown in Table 2, it was found that the efficiency of the surface increases by activating it with hydrochloric acid, as it works to increase the active sites on the surface and increase the surface area, thus increases its efficiency in removal pollutants from aqueous solution.[15]

CONCLUSION

White marble appeared to be an excellent alternative for the elimination of AMX drug from aqueous solution. The adsorption process offers important advantages owing to the utilization of natural adsorbents, like white marble waste for the removal of AMX drug, due to easy availability, ease of operation low cost, ecological nature, ease of design, flexibility, and great affinity for the drug. The removal percentage and adsorption capacity of the removal drug increase with increasing surface area, and equilibrium time, decreasing with an increase of concentration AMX drug solution and the adsorption capacity (Qe mg/g) decreasing with an increase of weight of white marble. The adsorption contact time of AMX drug reaches 60 minutes. The best value of Qe (mg/g) was found at a solution temperature 40°C. Exclusively effective parameters give the best fitting of model Freundlich better than model Langmuir.

REFERENCES

1. Gupta, VK, Srivastava SK & Mohan D, *Equilibrium uptake, sorption dynamics, process optimization, and column operations for the removal and recovery of malachite green from wastewater using activated carbon and activated slag.* Industrial and Engineering Chemistry Research, 1997. 36: 2207–2218.
2. Kamari Y, and Ghiaci M, *Preparation and characterization of ibuprofen/modified chitosan/TiO2 hybrid composite as a controlled drug-delivery system,.* Microporous Mesoporous Mater, 2016. 234: 361–369.
3. Mohamed EM , Abdel M, Shaimaa RS, and Hanem AM, *Promoted removal of metformin hydrochloride anti-diabetic drug from water by fabricated and modified nanobiochar from artichoke leaves.* Sustainable Chemistry and Pharmacy, 2020. 18: 100336.
4. García-Uriostegui L, HIM-O TA, Camacho-Villegas PH, Lugo-Fabres and Toriz G, *Synthesis and characterization of mesoporous silica-g-poly (hydroxyethylmethacrylate) nanohybrid particles as a drug delivery system.* Mater. Chem. Phys, 2022. 283: 126048.
5. Mahamda HA and AA Al Alwany AA, Influence of Syphilis Infection on Abortions in Iraq. Journal of Communicable Diseases, 2022, 54(4): 41-45
6. Xinyou M, Lan W , Shiqing G, Yanyan D , Yunqing Z , Chuanyi W , and Eric L, *Synthesis of a three-dimensional network sodium alginate–poly(acrylic acid)/attapulgite hydrogel with good mechanic property and reusability for efficient adsorption of Cu2+ and Pb2+.* Environmental Chemistry Letters, 2018. 16: 653–658.
7. Ihaddadene B, Tifouti L, Al-Dujaili AH, and Gherraf N, *Enhancing batch adsorption capacity of bentonite, kaolinite and their organomodified forms for phenol removal.* International Journal of ChemTech Research, 2015, 8(4) 1749-1762
8. Hanandeh AE, Abu-Zurayk RA, I Hamadneh, and AH Al-Dujaili, *Characterization of biochar prepared from slow pyrolysis of Jordanian olive oil processing solid waste and adsorption efficiency of Hg2+ ions in aqueous solutions.* Water Science and Technology, 2016. 74(8): 1899-1910.
9. Hamadneh, I, RA Abu-Zurayk, A Aqel, A Al-Mobydeen, L Hamadneh, Y Al-Dalahmeh, F Hannoon, R Albuqain, S Alsotari, and AH Al-Dujaili, *Impact of H3 PO4-activated carbon from pine fruit shells for paracetamol adsorption from aqueous solution.* Desalination and Water Treatment, 2022. 264: 293-306.
10. Bentarfa, D, ML Sekirifa, M Hadj-Mahammed, D Richard, S Pallier, B Khaldoun, and H Belkhalfa, *Characterization of activated carbon prepared from date palm fibers by physical*

activation for the removal of phenol from aqueous solutions. Desalination and Water Treatment, 2021. 236: 190-202.

11. Le Phuong Hoang , TMPN, Huu Tap Van d, Murat Yılmaz , Trung Kien Hoang ,Quang Trung Nguyen , Thi Mai Huong Vi ,Luong Thi Quynh Nga ,Show more, *Removal of Tetracycline from aqueous solution using composite adsorbent of ZnAl layered double hydroxide and bagasse biochar.* Environmental Technology & Innovation, 2022. 28: 102914.
12. Aljeboree, AM, NM Hameed, HD Saleem, H Jasem, ES Abood, AG Abdulrazaq, AKO Aldulaim, and AF Alkaim, *Removal of Pollutants from Aqueous Solutions by using Natural Surfaces (Cotton) as a Model for Reusability and Highly Adsorbent Surface.* International Journal of Drug Delivery Technology, 2022. 12(2): 583-587.
13. Ventura Castillo Ramos, JRU, Antonio Ruiz Sánchez, María Victoria López Ramón,and Manuel Sánchez Polo, *Marble Waste Sludges as Effective Nanomaterials for Cu (II) Adsorption in Aqueous Media.* Nanomaterials, 2022. 11(9): 2305.
14. Ventura Castillo Ramos, JRU, Antonio Ruiz Sánchez, María Victoria López Ramón, Manuel Sánchez Polo, *Marble Waste Sludges as Effective Nanomaterials for Cu (II) Adsorption in Aqueous Media.* Nanomaterials, 2021. 9: 2305.
15. Alkaim, AF and AM Ajobree, *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. Dhiraj Mehta, PM, Suja George, *Utilization of marble waste powder as a novel adsorbent for removal of fluoride ions from aqueous solution.* Journal of Environmental Chemical Engineering 2016. 4(1).
17. Leili Mohammadi, HK, Abolfazl Asghari, Amin Mohammadpour, Mohammad Golaki, Abbas Rahdar, and George Z. Kyzas, *Removal of Amoxicillin from Aqueous Media by Fenton-like Sonolysis/H2O2 Process Using Zero-Valent Iron Nanoparticles.* Molecules. , 2022. 27(19): 6308.
18. Aljeboree, AM, ZD Alhattab, US Altimari, AKO Aldulaim, AK Mahdi, and AF Alkaim, *Enhanced removal of amoxicillin and chlorophenol as a model of wastewater pollutants using hydrogel nanocomposite: Optimization, thermodynamic, and isotherm studies.* Caspian Journal of Environmental Sciences, 2023. 21(2): 411–422.
19. Zahra Seifollahi, AR-K, *Amoxicillin Extraction from Aqueous Solution by Emulsion Liquid Membranes Using Response Surface Methodology.* Journal of Chemical Technology & Biotechnology, 2019. 42(1): 156-166.
20. Elveny M, Alrazzak NA, Aljeboree AM, Alkaim AF, Ebadi AG, Substituent effects of fused Hammick germylenes: Estimating the stability and reactivity using density functional theory, Journal of Physical Organic Chemistry, 2021, 34 (11), art. no. e4262, DOI: 10.1002/poc.4262
21. Samiyammal P, Kokila A , Arul L , R Rajakrishnan , S Rengasamy , S Ragupathy , M Krishnakumar , and R Vasudeva *Adsorption of brilliant green dye onto activated carbon prepared from cashew nut shell by KOH activation: Studies on equilibrium isotherm.* Environmental Research, 2022. 212: 113497.
22. Qingmei Meng , YZ, Di Meng , Xinpeng Liu , Zijian Zhang , Peiling Gao , Aiguo Lin , Lian Hou, *Removal of sulfadiazine from aqueous solution by in-situ activated biochar derived from cotton shell.* Environmental Research, 2020. 191: 110104.
23. Shweta , S, S Gaurav , K Amit, S Tahani , M Naushad , A Zeid, and J Florian, *Adsorption of cationic dyes onto carrageenan and itaconic acid-based superabsorbent hydrogel: Synthesis, characterization and isotherm analysis.* Journal of Hazardous Materials, 2022. 421(5): 126729.
24. Aljeboree, AM, SM Essa, ZM Kadam, FA Dawood, D Falah, and AF Alkaim, *Environmentally Friendly Activated Carbon Derived from Palm Leaf for the Removal of Toxic Reactive Green Dye.* International Journal of Pharmaceutical Quality Assurance, 2023. 14(1): 12-15.
25. Al Bakain, RZ, RA Abu-Zurayk, I Hamadneh, FI Khalili, and AH Al-Dujaili, *A study on removal characteristics of o-, m-, and p-nitrophenol from aqueous solutions by organically modified diatomaceous earth.* Desalination and Water Treatment, 2015. 56(3): 826-838.
26. Farabi Temel , M, SezenKucukcongar, *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.
27. Tayebeh E, Navid N, Mohammad H.E., and Masoumeh T., *Characterization and absorption studies of cationic dye on multi walled carbon nanotube–carbon ceramic composite.* Journal of Industrial and Engineering Chemistry 2027. 46: 35–43.
28. Ahmed Adam, OEA and AH Al-Dujaili, *The removal of phenol and its derivatives from aqueous solutions by adsorption on petroleum asphaltene.* Journal of Chemistry, 2013.
29. Li, Y, H Xiao, M Chen, Z Song, and Y Zhao, *Absorbents based on maleic anhydride-modified cellulose fibers/diatomite for dye removal. .* J. Mater. Sci., 2014. 49: 6696–6704.
30. Alhattab, ZD, AM Aljeboree, MA Jawad, FS Sheri, AKO Aldulaim, and AF Alkaim, *Highly adsorption of alginate/ bentonite impregnated TiO2 beads for wastewater treatment: Optimization, kinetics, and regeneration studies.* Caspian Journal of Environmental Sciences, 2023. 21(3): 657 - 664.
31. Abbasi FS, and Golmohammadi F, *Removal of cadmium from aqueous solution by nano composites of bentonite/TiO 2 and bentonite/ZnO using photocatalysis adsorption process.* Silicon, 2020. 12: 2721–2731.
32. Hussain, NA, A Taifi, OKA Alkadir, NH Obaid, ZM Abboud, AM Aljeboree, ALA Bayaa, SA Abed, and AF Alkaim. *Role of Pomegranate peels as a activated carbon for removal of pollutants*. in *IOP Conference Series: Earth and Environmental Science*. 2022.
33. Honglin , Z, C Sunni , D Hanyi, H Jie , and L Yangchao *Removal of anionic and cationic dyes using porous chitosan/carboxymethyl cellulose-PEG hydrogels: Optimization, adsorption kinetics, isotherm and thermodynamics studies.* International Journal of Biological Macromolecules, 2023. 231(15): 123213.
34. Choy, KKH, JF Porter, and G McKay, *Langmuir Isotherm Models Applied to the Multicomponent Sorption of Acid Dyes from Effluent onto Activated Carbon.* J.Chem. Eng. Data. , 2000. 45 575-584.
35. Aljeboree, AM, GS Hamid, AA Katham, MM Abdulkadhm, HA Lafta, AMB Al-Dhalimy, AF Alkaim, and SA Abed. *Highly adsorbent surface from watermelon peels : as non-conventional low-cost sorbent ; Equilibrium and Recycle study*. in *IOP Conference Series: Earth and Environmental Science*. 2022.