RESEARCH ARTICLE

Removal of Amino Drug from Aqueous Solution by Clay and Study of Optimum Condition Colorimetric Determination of Amino Drug Using Reagent: Stability and Higher Sensitivity

Aseel M. Aljeboree*, Sadiq A. Karim, Ayad F. Alkaim

Department of Chemistry, College of Sciences for Girls, University of Babylon, Hilla, Iraq

Received: 29th December, 2021; Revised: 24th January, 2022; Accepted: 09th Febraury, 2022; Available Online: 25th March, 2022

ABSTRACT

One of the most dangerous pollutants in water are pharmaceutical, which were treated with the use of easy, simple and inexpensive. The adsorption process depends on the use of available and inexpensive surfaces. In this study, it relied on the use of clay (Bentonite), where several factors were studied, including the effect of surface weight, the effect of drug concentration and function. The acidity isotherms were also studied, and it was based on measuring the concentration of the residual from the adsorption process with the formation of the colored complex. In this paper, a fast, inexpensive, simple and highly sensitive colorimetric method was used for the determination of the amino drug (4-Aminoantipyrine 4AAP). A new azo dye was prepared by the diazanium process in the presence of acidic medium and the formation of diazanium salt, which reacts with a reagent in the presence of an alkaline medium to form azo dye with violet color. Several factors have been studied to develop the color of the compound and to obtain the best absorption and high sensitivity. Among these factors are the effect of reagent volume, effect of base volume and quality, effect of temperature, effect of addition order and type of reagent. This colorimetric method is very suitable for the determination of 4AAP in commercial pharmaceutical formulations such as.tablets and capsules to give a stable color for three hours. This method is characterized by its color accuracy and high accuracy, as well as high sensitivity for drug estimation.

Keyword: 4 Aminoantipyrine, Adsorption, Amino drug, Azo dye, Clay, Colorimetric, Diphenylamine, Pharmaceutical, Spectrophotometry

International Journal of Pharmaceutical Quality Assurance (2022); DOI: 10.25258/ijpqa.13.1.14

How to cite this article: Karim SA, Aljeboree AM. Removal of Amino Drug from Aqueous Solution by Clay and Study of Optimum Condition Colorimetric Determination of Amino Drug Using Reagent: Stability and Higher Sensitivity. International Journal of Pharmaceutical Quality Assurance. 2022;13(1):66-70.

Source of support: Nil.

Conflict of interest: None

INTRODUCTION

Over the past few years, personal care products and drug have become one of the most dangerous pollutants, and because of their continuous presence in the aquatic environment on a large scale, they are widely used to care for the health of human and animal life.Personal care products are widely found in groundwater, surface water, drinking water and sewage water in very low concentrations.[1-3] Therefore, one of the most important problems that developing countries suffer from is pollution with personal care products.pharmaceuticals are used in human medicine and veterinary complexes with great consumption in all countries. Pharmaceutical preparations are also used to increase biological efficacy.[3-6] One of the most important techniques used to get rid of pollutants in westwater, such as the oxidation process, the photodegredation process, and the adsorption process. The adsorption process is considered one of the most important techniques used to treat pollutants in water, especially pharmaceutical pollutants, which exist in very low concentrations that are difficult to remove easily, as they depend on the use of available, easy to prepare and inexpensive surfaces.[7,8] In general, the therapeutic importance of a drug for 4AAP requires the improvement of a new, simple, sensitive, inexpensive and rapid method, clinical monitoring and industrial quality control. Polarization and fluorometry.[3,9-11] This study was based on the development of the colorimetric method using a simple, easy, fast and inexpensive method, which is the method of nitrification by the formation of diazaium salt in an acidic medium. Several factors were studied, including the volume of the reagent, the volume and type of the base and reagent to development of the color complex.

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

EXPERIMENTAL DETAILS

Synthesis of Azo Dye.

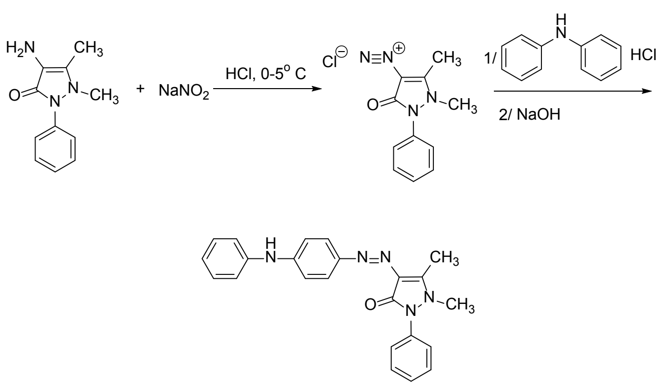
A volume (10 mL) of 4AAP drug and the same volume of hydrochloric acid were taken, and the mixture was collected in a conical flask of (100 mL). After that, the mixture was cooled in an ice bath at a degree (0°C) and then sodium nitrate (0.68 g, 0.0099 mol) was added, leaving the addition drop by drop at a temperature (25°C). After the formation of the disanium salt, the reagent was added to concentrate ((1.663 g, 0.00984 mol)) and hydrochloric acid in the volume of (10 mL) drop by drop with continuous stirring at room temperature give the powder violet color for the azo dye as appear in Figure 1.

REAGENTS AND MATERIALS

A 4-Aminoantipyrine stander solution (100 mg/L): The stoke solution of 4-Aminoantipyrine was prepared by means of 0.1 g dissolving in 100 mL of D.W. dilutions Serial through D.W were made to cover the range working.

Preparation of Clay

Bentonite clay was obtained from a geological survey, where the clay was ground by a special mill and then washed with distilled water several times to get rid of (CO_2) and the clay was activated, washed with hydrochloric acid at a concentration (0.1N) and then re-washed with distilled water several times until reaching (pH = 7) and finally it was dried at a temperature (110) about 24 hours and the powder used in the experiment was obtained.



Scheme 1: Synthesis of azo dye and reaction Coupling with reagent to give violet color for the azo dye

Spectrophotometric Determination of Drug 4-Aminoantipyrine

Accurately measured suitable volume of 4-Aminoantipyrine was transported from solution to 10 mL conical flasks, that can diluted to addition 3 mL 4-Aminoantipyrine, each one having 3.0 mL of reagent (1%) diphenylamine in basic medium, After 5 minutes through mixing, to give violet color and completing the volume to 10 mL via D.W, the values of absorbance were measured at 560 nm against the blank reagent that result in Figure 1.

Adsorption Studies

Study the optimum condition of adsorption like the effect of drug concentration (10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90 and 100 mg/L) were used and the effect of clay Bentonite weight of clay (0.05,0.1,0,2,0.3,0.4,0.5 and 1 g) and the effect of pH (2,4,6,8,10). at room temperature. Using the following equation to determination adsorption efficiency at equilibrium:

$$qe = \frac{\text{Vsol.}\,(\text{Co} - \text{Ce})}{\text{m}} \quad \ldots (1)$$

The adsorption efficiency and removal(R%) of the 4AAP on the adsorbents were calculate in equations:

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

RESULTS AND DISCUSSION

FTIR

Through infrared technology, the azo dye was identified, where it was observed from the Figure 2 of the (FTIR) spectrum that a strong adsorption band appeared at the site 1650.95 cm^{-1} indicating the appearance in the carbonyl group pyrazoline

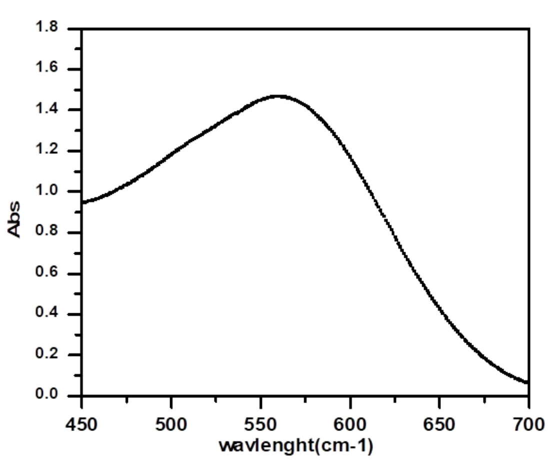


Figure 1: Absorption spectra of (25 $mg.L^{-1}$) solution 4-Aminoantipyrine

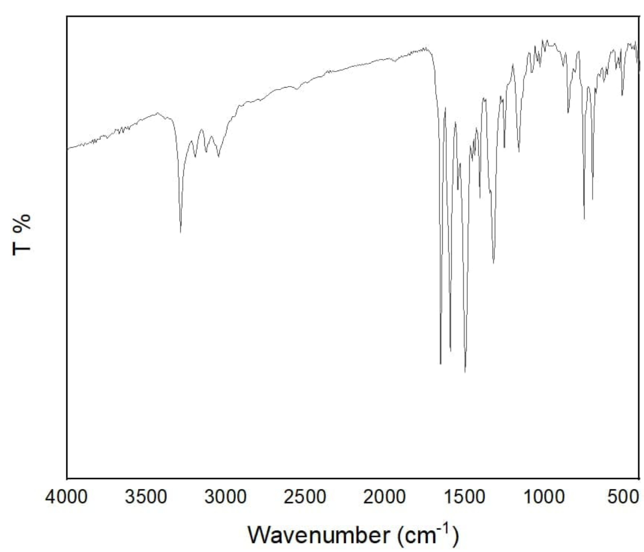


Figure 2: FT-IR for Compound azo dye

ring, and a strong absorption band due to the aromatic ring at 1588.24 cm^{-1} C = C stretcher, a weak absorption band indicated the -N = N group at 1497.67 cm^{-1} and a weak absorption band appeared due to the -NH group at 3287.47 cm^{-1},[12] as appear in Figure 2

Effect of Volume of Reagent

Absorbance measuring of solution having a several volume of reagent (1–5 mL). The influence of various volumes of reagent was studied. The one which gave the maximum absorbance and best intensity of the color complex by using 2 mL of reagent solutions was selected for further utilize. The data look in Figure 3. Although Increased reagent volume had no pronounced influence on formation complex, thus hence 2 mL was selected for further studies because it gives higher absorbance and the best sensitivity.[13-15]

Effect of Time on the Stability of Colored Complex

There action time of the optimum condition and color dye stability were also studied. As appear in Figure 4. Complete the intensity color was attained then 3 minutes of mixing of the complex. remains the absorbance higher stability for 2 hours then slowly decay among 3–5 hours. Therefore, 3 min was chosen as a waiting time in this study.[16-19]

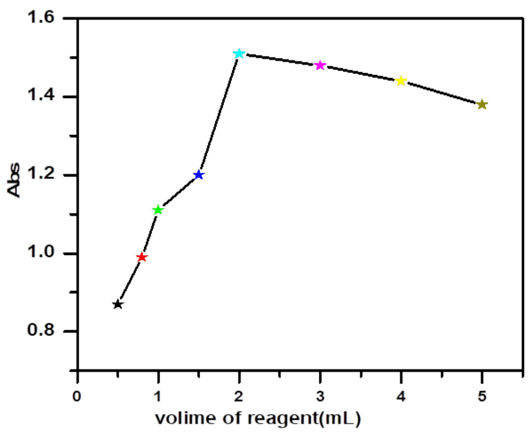


Figure 3: Effect of the volume of reagent

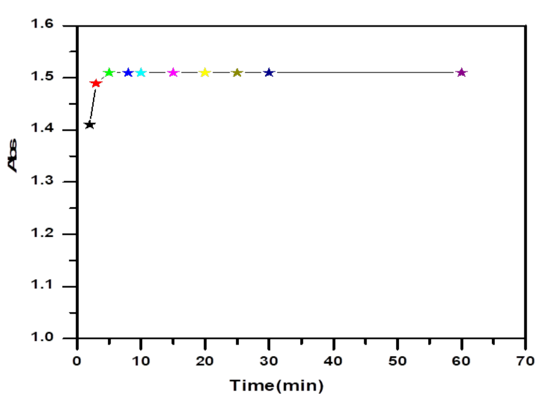


Figure 4: Effect of time on the stability of colored complex

Effect of Temperature

Temperature is one of the most important basic factors by which the stability of the color of the complex formed under the conditions is determined by the size of the reagent, the type of base and the type of the reagent. The range of temperatures (10–60°C) was used as shown in the Figure 4, where it was noted that the best temperature for color stability was at 25°C Where it gives the best absorbance and the best sensitivity, it is also found that the higher the temperature, the absorbance will decrease to give the least sensitivity,[20-22] as shown in the Figure 5.

Effect Volume of the Base

One of the most important factors affecting the stability of the color of the formed complex is the type and size of the base used, so three types of base (NaOH, Na2CO3, NaHCO3) were used with a concentration (0.1 N) as appear in Table 1 where it was found that the best sequence of the base was (NaOH). After determining the best base used, different volume of this base were used.[20-22] It was found that the best volume was (0.8 mL), which gave the greatest absorption and the best sensitivity, as shown in the Figure 6.

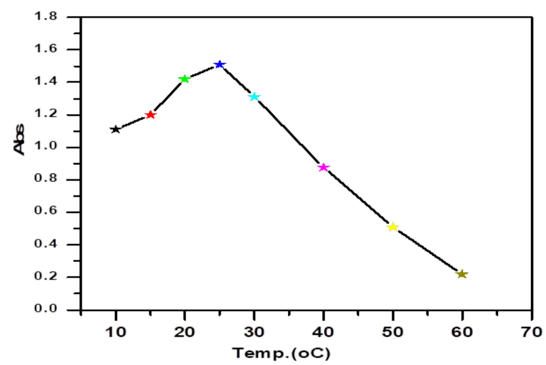


Figure 5: Effect of different temperature solution on the sensitivity and stability color complex

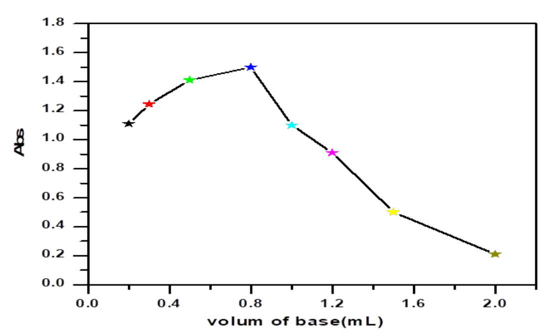


Figure 6: Effect of the different volume NaOH adding to drug

Table 1: Effect of the Kind base adding to drug

Type of base	*Absorbance*
Na_2CO_3	0.044
NaOH	0.155
NH4OH	0.029

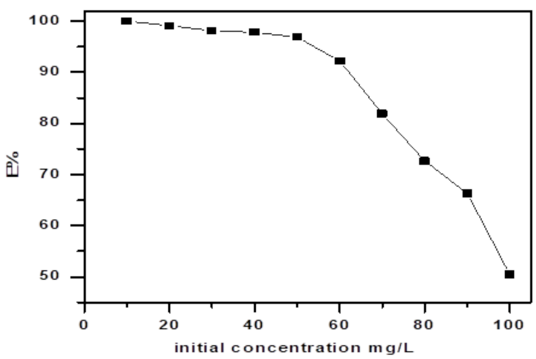


Figure 7: Effect of the initial concentration of amino drug on to removal percentage %under optimum conditions of 0.5 gm mass of clay, 1 hour, 0.5 gm clay.

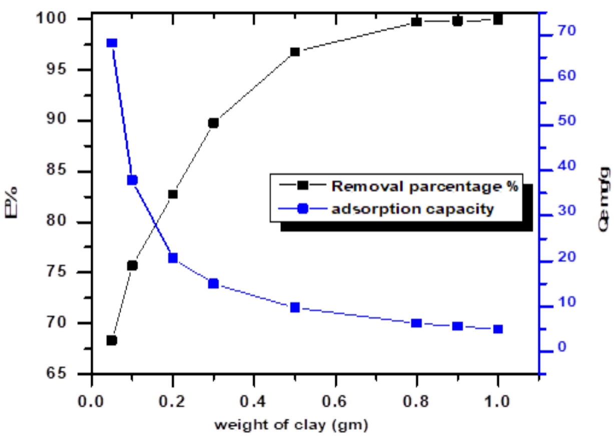


Figure 8: Effect of weight of clay on to removal amino drugunder optimum conditions of 50 mg/L initial concentration of amino drug, 1 hour, pH 6.

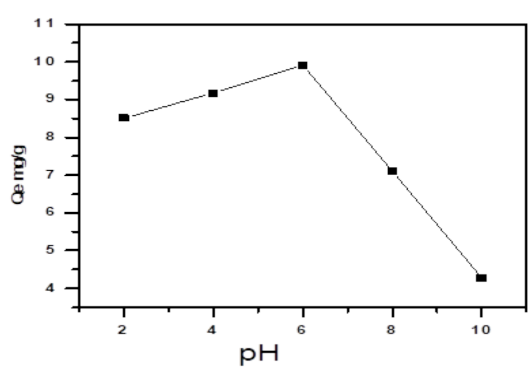


Figure 9: Effect of pH onto Removal amino drug was extracted under optimum conditions of 50 mg/L initial concentration of amino drug, 1 hour, 0.5 gm clay.

Effect of Different Parameter of Adsorption Presses

Effect of Concentration of Amino Drug

Figure 7 shows the effect of different concentrations of the amino drug under experimental conditions of clay weight 0.5 gm, equilibrium time 1 hours and solution of pH 6. It was found that by increasing the concentration of the amino drug, the removal percentage decreases significantly from (98.125 to 51.123%), but the opposite is observed by the adsorption efficiency where it increases with increasing concentration of the amino drug. This depends on the fullness of all the active sites of the surface.[22-24]

Effect of Weight of Clay Surface

The effect of clay weight on the removal of the amine drug was studied by taking different weights of clay (0.05 to 1 g) under experimental conditions from the time of equilibrium 1 hour and concentration of the amine drug (50 mg/L) and solution pH 6. found when the weight of clay increase the removal percentage% increase from (68.653 to 99.97%) because the effective sites until saturation is reached, but the adsorption efficiency decreases significantly with increasing surface weight from (68.23 to 5.344 mg/g)[25] this result appear in Figure 8.

Effect of pH

The effect of the pH solution on the amino drug has a key role in the adsorption process, where the range (3–10) at concentration (50 mg/L), equilibrium time 1 hour and temperature 25°C were studied. The result appear the best removal capacity at pH normal (10.122 mg/g)%.[26-30] It was observed in the basic medium that the adsorption efficiency decreased significantly due to the repulsion force between the positive amine drug and the surface this data appear in Figure 9.

CONCLUSION

In this study, the proposed technique is simple, characterized by stability and high sensitivity, as it gives absorption at 560 nm by using a UV-V spectrophotometer using the optimal experimental conditions to experiment. And considering the reagent has a very important role in stabilizing the color of the complex formed and increasing the sensitivity, as the greater the volume of the reagent, the greater the absorption. It has a negative effect and behavior as the color was stable and stable at room temperature for three hours. Several factors were studied for the adsorption process, and it was found that with the increase in the concentration of the amino drug, the removal percentage % decreases, and with the increase weight of the clay, the removal percentage increases and decrease adsorption efficiency and the best pH 6.

REFERENCE

1. Thomas K, Mitchner H, Colorimetric Determination of Phenylephrine Using 4-Aminoantipyrine. Journal of Pharmaceutical Sciences, 1963. 52(8): p. 802-803.
2. Atia NN, Mostafa AM, Ahmed IH, Walid EE, Development of two spectrophotometric methods for quantification of certain anti-depressant drug in pure, pharmaceutical formulation and application to content uniformity testing. Microchemical Journal, 2019. 147: p. 1048-1054.
3. 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): p. 31-37.
4. Gupta AJ; Colorimetric Determinations of Chlorpheniramine Maleate, Ephedrine Hydrochloride, and Guaiacolsulfonate Potassium in a Cough Syrup. Journal of Pharmaceutical Sciences, 1975. 64(12): p. 2001-2002.
5. Hassouna, M, Issa YM, and Zayed AG, Spectrophotometric Determination of Furosemide Drug in Different Formulations using Schiff 's Bases. Forensic Research and Criminology International Journal 2016. 1(6): p. 10.15406/frcij.2015.01.00036.
6. Esraa MR, Aseel MA, Ayad FA, Sensitive and Simple Method for the Spectrophotometric Determination of Paracetamol Drug Using Oxidative Coupling. International Journal of Psychosocial Rehabilitation, 2020. 24(05): p. 1475-7192.
7. Mhammed A, Atyaa AA,, ND Radhy, Jasim A., 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): p. 062023.
8. Aljeboree, AM, Removal of Vitamin B6 (Pyridoxine) Antibiotics Pharmaceuticals From Aqueous Systems By ZnO. International Journal of Drug Delivery Technology 2019. 9(2): p. 125-129.
9. Daharwal SJ, Development and Validation of UV Spectrophotometric Method for Simultaneous Estimation of Diazepam and Propranolol in Bulk Drug and its Formulations. Asian J. Pharm. Ana., 2013 3(1): p. 20-23.
10. Ayad FA, Adsorption and Photocatalytic Degradation of Pharmaceutical Amoxicillin using TiO2 Nanoparticles in Aqueous Solutions: Oxidative Coupling as Spectrophotometric Method International Journal of Advanced Science and Technology 2020. 29(5): p. 5480 - 5487
11. Safaa HG, Makarim AM, Aseel MA, Layth SJ, Selective Spectrophotometric Determination of 4-amino Antipyrine Antibiotics in Pure Forms and their Pharmaceutical Formulations. International Journal of Drug Delivery Technology, 2021. 11(2): p. 371-375.
12. Mohammed AJ,Nadher DR, Role of Sodium Alginate-g-poly (Acrylic acid-fumaric acid) Hydrogel for Removal of Pharmaceutical Paracetamol from Aqueous Solutions by Adsorption International Journal of Pharmaceutical Quality Assurance, 2021. 12(3): p. 202-205.
13. Akhond M, Absalan G; Ershadifar H, Highly sensitive colorimetric determination of amoxicillin in pharmaceutical formulations based on induced aggregation of gold nanoparticles. Spectrochim. Acta A, , 2015. 143: p. 223-229.
14. Patil R, et al., Validated HPLC Method for Concurrent Determination of Antipyrine, Carbamazepine, Furosemide and Phenytoin and its Application in Assessment of Drug Permeability through Caco-2 Cell Monolayers. Sci Pharm., 2012. 80: p. 89-100.
15. Tulasamma P; and Venkateswarlu P, Spectrophotometric determination of nifedipine in pharmaceutical formulations, serum and urine samples via oxidative coupling reaction. Arabian Journal of Chemistry. 9: p. S1603-S1609.
16. Adegoke OA, Thomas OE, and Emmanuel SN, Colorimetric determination of olanzapine via charge-transfer complexation with chloranilic acid. Journal of Taibah University for Science, 2016. 10(5): p. 651-663.
17. Gowda JI, Electrochemical behavior of 4-aminophenazone drug at graphite pencil electrode and its application in real samples. Ind. Eng. Chem. Res., 2012. 51: p. 15936-15941.
18. Aljeboree, AM, Spectrophotometric and Colorimetric Determination of Pharmaceutical by Oxidative Coupling Reaction: A Review. Sys Rev Pharm 2020. 11(4): p. 609 615.
19. Aljeboree AM and Alshirifi AN, Oxidative coupling of Amoxicillin using 4-Aminoantipyrine: Stability and higher sensitivity. Journal of Physics: Conference Series, 2019. 1294(5): p. 052001.
20. Mohamed, GG, Spectrophotometric determination of ampicillin, dicluxacillin, flucloxacillin and amoxicillin antibiotic drugs: ion-pair formation with molybdenum and thiocyanate. Journal of Pharmaceutical and Biomedical Analysis, 2001. 24(4): p. 561-567.
21. Aseel MA, Colorimetric determination of Amoxicillin using 4-Aminoantipyrine and the effects of different parameters. Journal of Physics: Conference Series, 2019. 12(5): p. 052067.
22. 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: p. 012064.
23. Amer M JA, Mohammed B. Alqaragully, Ayad F. Alkaim, Removal of toxic textile dyes from aqueous solution through adsorption onto coconut husk waste: Thermodynamic and isotherm studie. Caspian J. Environ. Sci. , 2021.
24. Aseel MA, Alkaim AF, Role of plant wastes as an ecofriendly for pollutants (Crystal Violet dye) removal from Aqueous Solutions Plant Archives 2019 19(2): p. 902-905.
25. Yahya AF , Nadher R, Removal of Metformin hydrochloride from Aqueous Solutions by using Carboxymethyl cellulose-g-poly(acrylic acid-co-acrylamide) Hydrogel: Adsorption and Thermodynamic Studies. IOP Conf. Series: Earth and Environmental Science 2021. 790: p. 012062.
26. Aljebore AM, Adsorption and Removal of pharmaceutical Riboflavin (RF) by Rice husks Activated Carbon. International Journal of Pharmaceutical Research 2019. 11(2): p. 255-261.
27. Waleed KA, Makarim AM, Layth SJ. Adsorptive Removal of Doxycycline from Aqueous Solution Using Graphene Oxide/Hydrogel Composite. International Journal of Applied Pharmaceutics, 2020. 12(6): p. 100-106.
28. Haitham MA, Mohammad NA, Ayad FA, Synthesis and Characterization of Nano-composite copolymer: Adsorption and Removal Studies of vitamin B12 from Aqueous Solutions. IOP Conference Series: Earth and Environmental Science, 2021. 790 p. 012057.
29. Layth SJ , Adsorption and removal studies of heavy metal Pb(II) on their Water Solution on adsorbent surface of Vinyl Alcohol/Chitosan-Graphene Oxide. IOP Conf. Series: Earth and Environmental Science 2021. 790: p. 012063.
30. Aseel MA, Ali L ,Hanadi MA, 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(3): p. 138-143