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REMOVAL OF AMOXICILLIN DRUG ONTO NANO COMPOSITES SURFACE USING ULTRASOUND ASSISTANCE

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Abstract

Antibiotics, an important type of pharmaceutical pollutant, have attracted many researchers to the study of their removal from aqueous solutions and amoxicillin(AMX) consider one of important types Antibiotics. In this study, Clay was developed and loaded on one type Carbon (sugar) to give (Clay /sugar Nano composites). Has been widely used as highly effective adsorbent for amoxicillin (AMX) drug because of its large specific surface area, high porosity, and favorable pore size distribution. Maximum adsorption capacities of 202.7 mg/g was reported for AMX, The influence of process variables (initial drug concentration, adsorbent mass and PH) on the removal of drug solution were investigated. The adsorption equilibrium was represented with Freundlich and Langmuir isotherm models. The equation was found to have the correlation coefficient value in very good agreement of AMX drug Langmuir models, while Freundlich equation was found to give a good correlation of drug.

Key words : Antibiotics, Amoxicillin, ultrasound, Nano composites, Clay, Adsorption, Removal, Isotherm.

Introduction

For many years, antibiotics have been a significant group of pharmaceuticals widely used to treat human and animal infectious diseases, on the one hand, and to increase agricultural products, on the other. veterinary medicine to treat diseases and infections, and as feed additives to promote growth and weight gain in livestock (Aseel M Aljeboree 2018; Aseel M. Aljeboree 2018; Aseel Musthaq Aljeboree 2018). Antibiotics may be excreted through urine, feces, and manure in both non-metabolized and metabolized forms, which then flow into surface water, groundwater, and drinking water through the water cycle. (KÃ¼mmerer 2009; F. Ferrag-Siagh 2013).

Amoxicillin (Fig. 1) is the only phenolic penicillin and a spectrum β-lactam antibiotic. β-Lactam antibiotics present a structure based on a β-lactam ring which is responsible for the antibacterial activity and variable side chains that explain the major differences in their chemical and pharmacological properties. It is usually chosen because it is better absorbed, following oral administration, than other β-lactam antibiotics (Ojani, Raoof *et al.*,; Uslu and Biryol 1999; Aljeboree and Alshirifi 2019).

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Clays are hydrous alum inosilicates composed of mixtures of fines-grained clay minerals, crystals of other minerals and metal oxides. Clays play an important role in the environment by taking up cations and anions through adsorption or ion exchange. They belong to low-cost sorbents. Clay can be modified to improve its sorption ability; one of the methods is the use of magnetic modification in which, e.g., modified Fe/Attapulgite clay (Aljeboree 2015), bentonite coated with iron can be obtained [4]. In this study was used one of the types clay to increase the percent removal (%) of the pharmaceuticals contaminants have been improved clay by adding one type Carbon (sugar) this considered from environmentally friendly materials.

Materials and Methods

Preparation of Clay /Sugar Nanocomposite

Nanocomposite was prepared using the hydrothermal process Fig. 2 for prepared of clay decorated one type

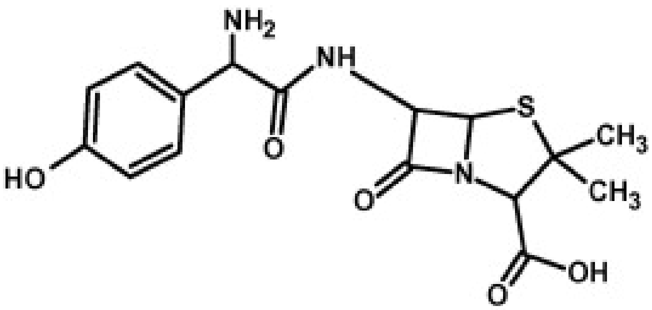

Fig. 1: The chemical structure of amoxicillin ((2S,5R,6R)-6-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid) (De Baere and De Backer 2007; Aseel M aljeboree 2018; Aljeboree and Alshirifi 2019).

carbon (Sugar), 4 g of homogenized clay in 150 ml distilled water, was added with 1g $FeCl_3$ powder, 2g Sugar, and 1g NaOH and mixing at 30 min by magnetic stirrers . Then was placed inside oven and the temperature of the oven was set to 180ºC for 24 after that the result powder separated from the solution and washed with distilled water several times with ultrasonic device until the pH of the wash became neutral (pH =7). Finally the products were dried for 24h at 80ºC in an oven. The products is (Clay/ Sugar) (black powder) .

Fig. 2: Stainless steel hydrothermal technique.

Adsorption experimental methods and measurements

The calibration curve, solutions of different concentrations for compound was prepared by serial dilutions. Absorbance values of these solutions were measured at the selected λmax value of AMX drug and plotted against the concentration values AMX in Fig. 3 the calibration curves in the concentration range that falls in the region of applicability of Beer-Lambert's law were employed. The effects of experimental parameters, adsorbent dosage (varied forms 0.01–0.15 g) pH (varied between 2–11), initial dye concentration (2–100 $mg.L^{-1}$), on the AMX drug adsorption were studied in a ultrasonic of operation for a contact time of 60 min. The effect of pH was studied by adjusting the pH of the drug solution by adding 0.1 N HCl or 0.1 N KOH. The solution and solid phase were separated by centrifugation at 2500 rpm for 10 min in a Hettich EB 21 centrifuge, repeated two times to ensure there is no particles scattered the absorbance measurements and analyzed using a UV–vis spectrophotometer (Shimadzu UV/Vis 1650 spectrophotometer, Japan) at a wavelength of 278 nm. The final Concentration of the solution was then determined from the calibration curve. The concentration retained in the adsorbent phase ($qe/mg.g^{-1}$) was calculated by using the following equation (A.A. Ensafi 2012):

$$qe = (C_o - C_e)\ V / W \quad ....(1)$$

Where C^o is the initial drug concentration and C_e is the equilibrium drug concentration

($mg.L^{-1}$), V is the volume of solution (L) and W is the mass of the adsorbent (g), also the

Percentage of dye removed (E%) from solution was calculated using the following equation:

$$E\ (\%) = (C_o - C_e) / C_o \times 100 \quad ....(2)$$

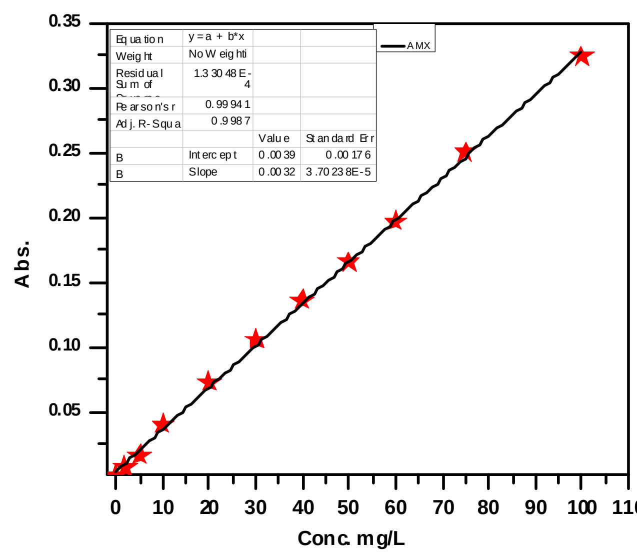

Fig. 3: Calibration curve for the *Amoxicillin (AMX).*

Results and Discussion

EDX and Field Emission Scanning Electron Microscopy (FE-SEM) analysis

Energy dispersive X-ray analysis were performed with the aim of identifying the elemental composition of each clay material after various stage of treatment and the results are presented in Fig. 4A

EDX is a versatile technique used for qualitative and semi-quantitative analysis, it was interesting to note that the iron present in the clay were increased in the presence of decorated Sugar and impetration of Fe_2O_3 (Gao, Yang *et al.*, 2016; Alkaim 2017; Enas M Alrobayi 2017).

The SEM images obtained at above 2000 times magnification (Fig. 4B) reveals the structure of the incorporated clay materials. The lamellar structures exhibited by the bentonite were clearly visible in the micrographs.

On the other hand, the micrographs of decorated Sugar samples (Fig. 4B)revealed the progressive changes in phase morphology owing to the presence of new irregular bulky particles on the surface. This resulted in increased protuberance and coarser surface texture which are absent before loading carbon (Gao, Yang *et al.*, 2016; Salman, Abdul-Adel *et al.*, 2016; Edathil, Pal *et al.*, 2018).

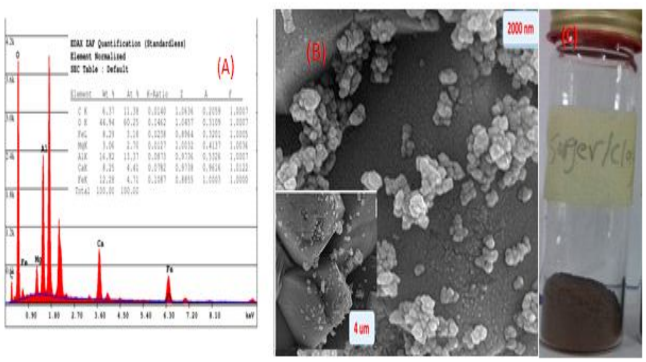

Fig.: 4: EDX analysis of (A) Clay/Sugar /Fe_2O_3 (B) SEM images Clay /Sugar /Fe_2O_3,(C) Actual image of Clay /Sugar /Fe_2O_3.

Effect of contact time

The adsorption of amoxicillin drug that derived at initial concentration of 50 mg L^{-1} was studied at different contact time (5-130 min). The drug adsorption an uptake was increased with time increased and reaches the contact equilibrium at 1hr (Fig. 5). In addition, the fast adsorption at the initial stage also may be due to the fact that a large number of surface sites are available for adsorption but after a lapse of time, the remaining surface sites are difficult to be occupied. This is because of the repulsion between the solute molecules of the solid and bulk phases, thus, make it take long time to reach equilibrium (Aseel M. Kadim Aljebori 2012; Aljeboree 2019).

Effect of Initial drug Concentration

The effect of drug Concentration on the percentage removal of the drug was investigated at different initial drug concentrations 2-100 mg/L as shown in Fig. 6. It is clear that the removal of drug was dependent on the concentration of the drug, and the process was faster at

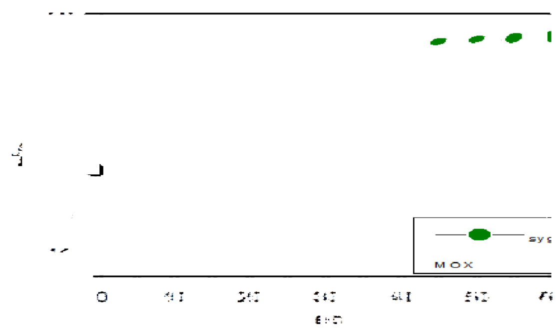

Fig. 5: Effect of contact time on removal of drug %, initial concentration = 50 mg/L, Temp. = 25°C, contact time 1 h, and mass of adsorbent 0.1 g/L).

higher concentrations. While the percent of removal decreases with increasing initial drug concentration from 84.37% at 2mg/L to 52.84% at 100 mg/L, the adsorption capacity increased from 3.375 mg/g to 51.75 mg/g, respectively. (D.K. Mahmoud 2012.; Gamal Owes El-Sayed 2013).

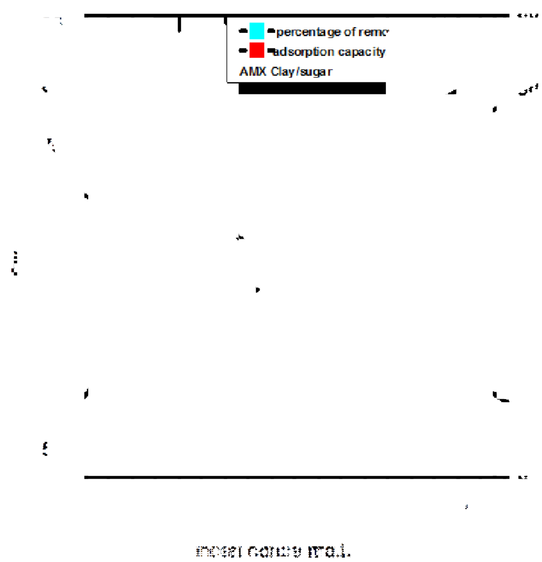

Fig. 6: Effect of initial concentration on the percent removal and amount of adsorbed AMX drug onto (Clay/Sugar) Temp. = 25°C, contact time 1 h, and mass of adsorbent 0.1 g/L).

Effect of Adsorbent Dose

The effect of the amount of the adsorbents was necessary in order to observe the minimum possible amount, which shows the maximum adsorption stoichiometric. The amounts of the adsorbent were varied from 0. 01 to 0.15 g/100 ml of (Clay/Sugar) nanoparticles. It is clear from (Fig. 7) increasing trend of efficiency is due to the increased active surface sites for adsorption and conglomeration of the adsorbent as the dosage of (Clay/Sugar) nanoparticles increases, enhancing the number of adsorption sites available for adsorption

(Ruwaida A Raheem 2016; Enas M Alrobayi 2017). The increase in the removal of drug with adsorbent dose due to the introduction of more binding sites for adsorption. The primary factor explaining this characteristic is that adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing the adsorbent dose (J.M. Salman 2010; Alqaragully 2014).

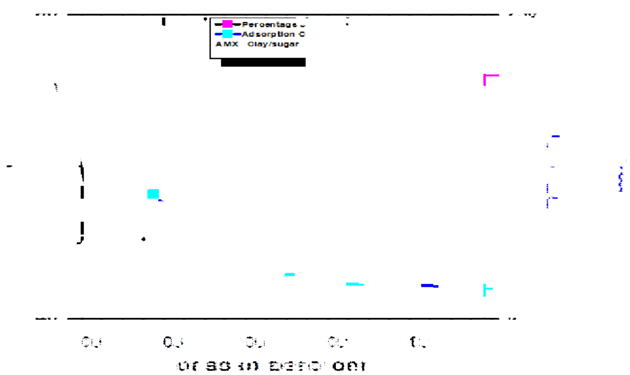

Fig. 7: Effect of mass adsorbent on adsorption a) AMX : experimental conditions: Temp. 25°C, pH 6, drug conc. 50 mg/L.

Effect of pH

Generally, pH of the reaction environment is one of the most important factors which should be considered in the study of adsorption processes with the effect on ionization of pollutants and the surface charge of adsorbent materials. In order to determine the effect of pH on the percentage of removal of AMX from aqueous solutions by adsorbent, 50mg/L AMX solutions were prepared in100 ml containers and the pH was adjusted between 2 and 11 (Fig. 8). The effects of selected adsorbents on the adsorption of AMX and the pH of the solution can be described with respect to the dissociation of AMX and surface charge of adsorbent. The isotropic point of 5.2 is expressed for AMX. Therefore, pH of the solution phase determines the ionization state of AMX molecules and depending on the pH values is in the range of positive, negative and neutral charge. (Jafari, Heidari *et al.*, 2018). The result showed that the highest removal efficiency was found to be 68.75 % at pH=6. Due to the isoelectric points of AMX, the charge of adsorbent has been positive and AMX has been negatively charged. It can be said that the adsorption factor of the AMX molecules is electrostatic forces that, AMX has been adsorbed on the adsorbent surface (A.B. Albadarin 2018). According to Ornelas *et al.*, 2010 (N.J. Ornelas 2010), similar to this phenomenon has been observed in the adsorption of AMX on activated carbon.

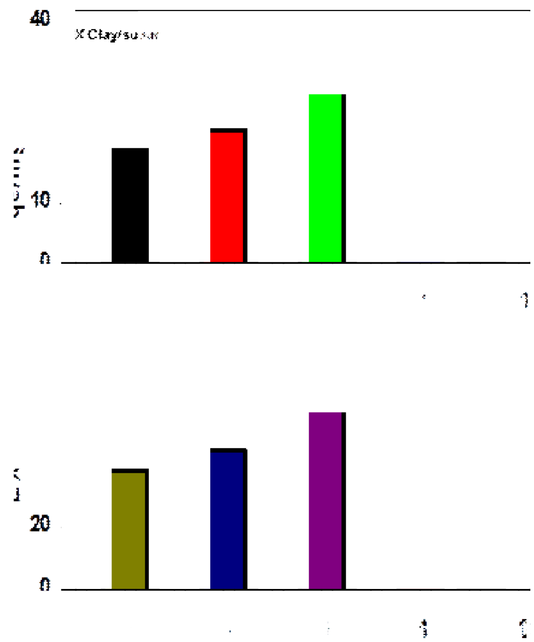

Fig. 8: Effect of solution pH on the percent removal and amount of adsorbed AMX drug onto (Clay/Sugar) initial concentration = 50 mg/L, Temp. = 25°C, contact time 1 h, and mass of adsorbent 0.1 g/L).

Models of Adsorption Isotherm

To investigate the parameters dependency of the adsorption capacity, two equilibrium models were analyzed, including Langmuir, Freundlich Isotherm.

Langmuir Isotherm

The Langmuir adsorption isotherm equation, expressed as follows requires for its applicability a mono-layered coverage on the surface of adsorbent. Eq. (3) (Langmuir 1918)

$$Qe = \frac{qmax\ KL\ Ce}{1 + KL\ Ce} \qquad ....(3)$$

The Langmuir isotherm was evaluated using the model Where Ce is the equilibrium concentration (mg/L), qe is the amount adsorbed at equilibrium (mg/ g), while, KL (L/ mg) are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The linear plots of qe against Ce, as shown in Fig. 9, reveal that the adsorption obeys Langmuir isotherm model for adsorbent. The values of KL, shown in (Table 1).

Freundlich Isotherm

The Freundlich isotherm was determined using the model. Where Kf and 1/n are Freundlich constants characteristics of the system, indicating the adsorption capacity and the adsorption intensity (ALQARAGULY 2013). The amount of solute adsorbed and concentration of solute in solution can be represented by qe and Ce respectively. Eq. (4) (Freundlich H 1939).

$$qe = K_f\, C_e^{1/n} \quad ....(4)$$

A plot of qe versus Ce is shown in Fig. 6, where the values of K_F and 1/n are determined from the intercept and slope of the linear regressions. As seen, a very high regression correlation coefficient was shown by the Langmuir model (R= 0.9908). This indicates that the Langmuir model was very suitable for describing the sorption of AMX drug on sugarcane stalks powder compared to Freundlich model (R=0.9895).

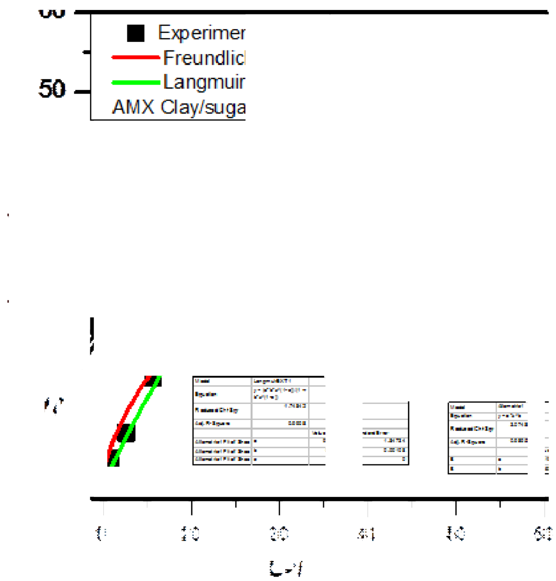

Fig. 9: Different adsorption isotherm models nonlinear fit for adsorption of AMX drug on (Clay/sugar) initial concentration = 50 mg/L, Temp. = 25°C, contact time 1 h, and mass of adsorbent 0.1 g/L).

Table 1: Langmuir and Freundlich, model isotherms parameters for AMX drug adsorbed on the surface of (Clay / Sugar) at 25°C.

AMX drug	Parameters	Isotherm models
1.8473 ±90.398	qm (mg.g^{-1})	Langmuir
0.00108 ±0.0287	K_L (L.mg^{-1})	
0.9908	R^2	
0.5245 ±5.1975	K_F	Freundlich
0.0301 ±0.6049	1/n	
0.9895	R^2	

Conclusion

In this study, one type of Carbon sugar loading Clay on the surface to produce by hydrothermal proses and the prepared nanocomposite was used as an adsorbent to remove AMX antibiotics from aqueous solutions. The optimal important parameters of absorption functions were obtained to be pH 6 Contact time 60 min, absorbance dose of 0.1 g at the AMX concentration of 50 mg/L. Adsorption of AMX was investigated on the Langmuir adsorption isotherms. Maximum adsorption capacity based on the Langmuir model was 52.8 mg/g. The study of adsorption isotherms showed that the adsorption process follows well the Langmuir adsorption isotherm with a regression coefficient of 0.9908. Clay/ Sugar nanocomposite It is economical and cost-effective because of the low cost of raw materials for the production of Clay/Sugar nanocomposite. Due to the high efficiency of the Clay/sugar nanocomposite in the removal of amoxicillin.

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