Plant Archives Vol. 19, Supplement 2, 2019 pp. 915-919 **e-ISSN:2581-6063 (online), ISSN:0972-5210**

ACTIVATED CARBON (AS A WASTE PLANT SOURCES)–CLAY MICRO/NANO-COMPOSITE AS EFFECTIVE ADSORBENT: PROCESS OPTIMIZATION FOR ULTRASOUND-ASSISTED ADSORPTION REMOVAL OF AMOXICILLIN DRUG

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Abstract

The combined ultrasonic assisted/nanoparticle based procedure was described for an economical and rapid removal of amoxicillin drug by clay decorated carbon nanocomposite (CDCN). The adsorbent was characterized with EDX and Field Emission Scanning Electron Microscopy (FE-SEM). Various operational parameters such as Contact time, initial drug concentration, mass dosage and pH, by use of (CDCN). In the adsorption of drug amoxicillin. Increasing the concentration of the adsorbent promoted an increase in the percentage of removal until saturation of the adsorbent. The equilibrium sorption capacity was minimum at pH 2 (12.5mg/g) and increased up to pH6, reached maximum (68.3 mg/g) 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 activated carbon this considered from environmentally friendly materials.

Key words: Pharmaceuticals, Amoxicillin, Nanocomposites, Adsorption, Ultrasound, Clay, Activated carbon.

Introduction

Pharmaceuticals are chemical products used in personal healthcare, medicated products, and cosmetics (Akhtar, Amin *et al*., 2015). As the quality of human life improves and the world population grows, the use of Pharmaceuticals is increasing rapidly. As a result, the contamination of surface and ground water has emerged as a serious problem in recent years, (Akhtar, Amin *et al*., 2015; Aljeboree and Alshirifi, 2018). Pharmaceuticals are frequently detected in treated wastewater arising from sewage treatment plants, from which they are not completely removed (Tambosi, Yamanaka *et al*., 2010; Aljeboree and Alshirifi, 2018). Many of these compounds are suspected to have adverse impact on humans and wild life (Stackelberg, Furlong *et al*., 2004).

Various physiochemical methods have been used for the removal of Pharmaceuticals. Including biodegradation (Liu, Zhu *et al*., 2017), biological treatments (Usharani, Lakshmanaperumalsamy *et al*., 2011), ion exchange(Chen, Chua *et al*., 2002), ozonation (Gomes, Costa *et al*.; Fabrao, Brito *et al*., 2019) chemical precipitation (Huisman, Schouten *et al*., 2006), advanced oxidation processes (AOPs), photo catalytic degradation(Hu, Lv *et al*., 2016), electrocoagulation, electrochemical technologies (Nariyan, Aghababaei *et al*., 2017), ultrafiltration membrane (Song, Yang *et al*., 2016) adsorption (Marques, 2017) have been used to treat pharmaceuticals. Among these methods, adsorption is the simplest, cheapest, and most versatile technique for holding these pollutants (Moro, 2017; Aljeboree and Alshirifi, 2018). Activated carbon(Xiong, Tong *et al*., 2017), carbon nanotubes (CNTs) (Zhao, Liu *et al*., 2016), mesoporous silica (Wu, Lai *et al*., 2016), clays (Uddin 2008), biochar, zeolite, resin(Kanakaraju, Kockler *et al*., 2015), chitosan (Kyzas, Fu *et al*.) and graphene oxide (Azhar, Abid *et al*., 2017) adsorbents have been effectively utilized to attract pharmaceutical pollutants from wastewaters.

The goal of this study was to esteem the efficacy of (CDCN) and new adsorbent to removing the drug AMX from aqueous solutions. Study effect different parameters such as, adsorbent dose, Effect of initial drug concentration, PH and adsorption isotherms were also analyzed**.**

Materials and Methods

Preparation of H_2SO_4-activated carbon (AC)

Coconut shells are obtained from the Iraqis local markets and were used as precursors. The collected sample was crushed very well, then washed exhaustively with deionized water to remove adhering dirt particles from the surface, then dried by oven (80 ^oC) for 24 h. followed by grinding and sieving in order to use particles size ranged between 1 mm and 2 mm**.** H_2SO_4/activated carbon sample (AC) was prepared via two steps: carbonization of dried precursor at 500 ^oC for 2 h in the absence of air using a muffle furnace (600 * 40 mm) at a rate of 10 ^oC/ min up to 500 ^oC. The carbonized sample was cooled and soaked with certain weight of H_2SO_4 (20 g of carbonized sample with 60 g of H_2SO_4 (50%)) in 100 ml distilled water for 24 h at 25^oC, followed by drying at 115^oC and finally activated at 500 ^oC for 3 h. The activated product was then washed with deionized water until the pH of the washing solution reached 6–7, then dried at 80 ^oC, for 24 h, crushed and sieved for experimental work (Aljeboree, Alshirifi *et al*., 2017)

Preparation of Clay /AC nanocomposite

Nanocomposite was prepared using the hydrothermal process Fig. 1 for prepared of clay decorated carbon nanocomposite (CDCN), 4 g of homogenized clay in 150 ml distilled water, was added with 1g $FeCl_3$ powder, 2g AC powder and 1g NaOH and mixing at 30 min by magnetic stirrers.

Fig. 1: Real image hydrothermal

Then was placed inside oven and the temperature of the oven was set to 180 ◦C 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 80◦C in an oven. The products is (CDCN) (black powder).

Adsorption Equilibrium Experiments

Stock solutions of the drug (0.1 g/1000 mL) were prepared, and the range of required concentrations was made by dilutions with distilled water. The initial tested concentrations of drug were (2, 5, 10, 20, 30, 40, 50, 60, 75 and 100 mg/L), The effect of initial solution pH on the drug adsorption by nanocomposite (CDCN) was studied at a concentration of 50 mg/L. and the pH was adjusted using 0.1 N KOH and 0.1 N HCl solutions by using an Orion 920A pH-meter with a combined pH electrode. pH-meter was standardized with NBS buffers before every measurement. The effect of mass dosage was studied by agitating in different masses (0.01, 0.025, 0.05, 0.075, 0.1 and 0.15 g), at 25 °C of 50 mg /L of nanocomposite (CDCN).

Ultrasound adsorption experiment was undertaken as follows: 100ml of 50 mg/L AMX was mixed thoroughly with 0.1g of nanocomposite (CDCN) at pH =6 at room temperature for 1hr ultrasound assuming that the equilibrium has reached. Finally, the sample was centrifuged and then analyzed for residual drug concentration by UV–vis spectrophotometer (Shimadzu UV/Vis 1650 spectrophotometer, Japan) at 278 nm. The amount of drug uptake by nanoparticles (CDCN) in each flask was calculated using the mass balance equation (Yang, Li *et al*. 2017).

$$q_e = \frac{C_0 - C_e}{W} \times V \qquad ....(1)$$

Where q_e is the amount of drug adsorbed by (CDCN) at equilibrium, C_o and C_e are the initial and final drug concentrations (M), respectively, V is the volume of solution (L), and W is the adsorbent weight (g). The drug percent removal (%) was calculated using the following equation: (Yang, Li *et al*. 2017)

$$E\% = \frac{C_0 - C_e}{C_0} \times 100 \qquad ....(2)$$

Result 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 Figures (2).

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 carbon and impegration of Fe_2O_3 (Gao, Yang *et al*., 2016).

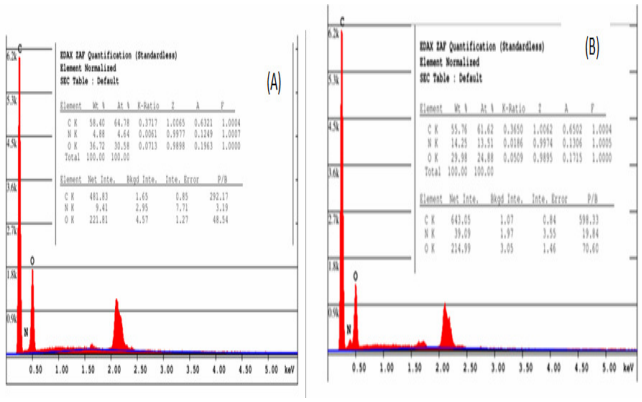

Fig. 2 : EDX analysis of (A) Clay , (B) AC/Clay /Fe_2O_3

The SEM images obtained at above 1000 times magnification (Fig. 3) 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 carbon samples (Fig. 3) 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; Edathil, Pal *et al*., 2018).

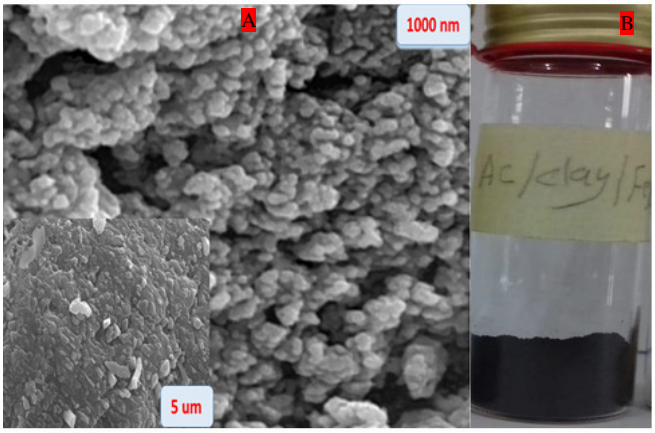

Fig. 3 : Actual and SEM images: (A) SEM images AC/Clay, (B) Actual image of AC/Clay.

Effect of agitation time

Agitation time is very important factor affecting the efficiency of adsorption. To study the removal efficiency of amoxicillin drug using nanocomposite (CDCN), a analysis is carried out using the previously determined optimum value of pH, nanocomposite (CDCN) dose and initial concentration. In this batch study samples were taken at different interval ranging from 5 to 130 minutes. It is clear from Fig. 4 that maximum adsorption occurs within 60 minutes. 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 The optimized value of agitation time is 60 minutes after which the adsorption becomes constant (Aljeboree, Alkaim *et al*., 2015; Khan, 2017).

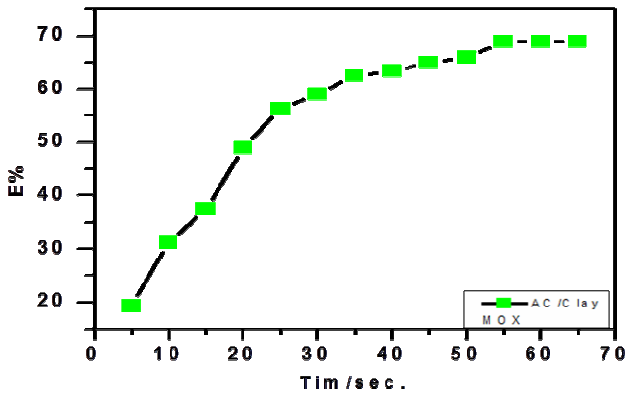

Fig. 4: Effect of contact time on removal of drug %, initial concentration = 50 mg/L, Temp. = 25°C, contact time 1 h, and mass of adsorbent 0.1 g/L).

Effect of initial drug concentration

The amount of adsorption for drug removal is highly dependent on the initial drug concentration. The effect of initial drug concentration depends on the immediate relation between the concentration of the drug and the available sites on an adsorbent surface. The effect of initial drug concentration on the removal of drug by nanocomposite (CDCN) is shown in Fig. 5 presents the removal efficiency versus drug concentration. The percentage of color removal efficiency decreases with increasing drug concentration. This indicates that there is a reduction in adsorption, due to the lack of available active sites required for the high initial concentration of the colored solution. The qe increased with the increase in initial drug concentration as the resistance to the uptake of drug from the solution decreases with the increase in drug concentration. The rate of adsorption also increases with the increase in initial drug concentration due to increase in the driving force (Bulut and Aydın 2006; Cardoso, 2011; Alkaim and Alqaragully, 2013; Kamil, Mohammed *et al*., 2016)

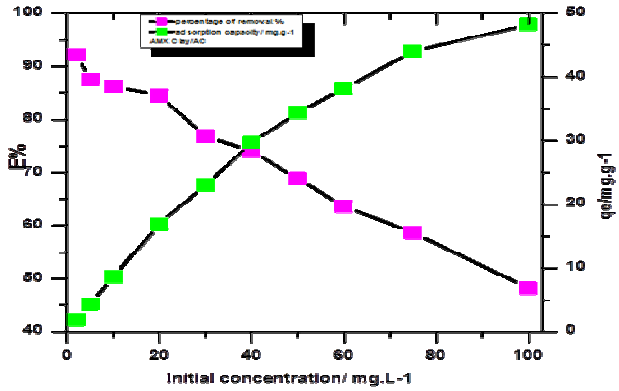

Fig. 5: Effect of initial concentration on the percent removal and amount of adsorbed AMX drug onto (CDCN) Temp. = 25°C, contact time 1 h, and mass of adsorbent 0.1 g/L).

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 0.001 to 0.15 g/100 ml of (CDCN) (Salman and Hameed 2010; Alqaragully 2014). It is seen from the Fig 6 that as the (CDCN) dose increases the adsorption efficiency increases and this is due to increase of surface area of the adsorbent. The optimum dose of (CDCN) that can be used in removal of AMX drug is 0.1 g/100 ml (Khan, 2017)

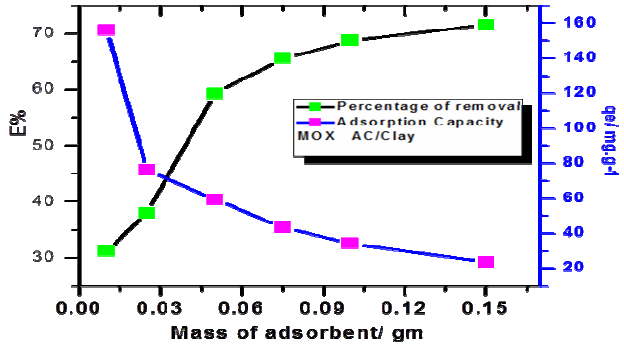

Fig. 6: Effect of mass amount of adsorbent (CDCN) on the percent removal and amount of adsorbed AMX drug , initial concentration = 50 mg/L, Temp. = 25°C, contact time 1 h.

Effect of solution pH on drug adsorption:

The effect of pH on adsorption of drug was studied within pH range 2–11. The adsorption of the drug on (CDCN) is largely affected by the solution pH (Cardoso NF 2011) .The optimum solution pH was found to be 6 (Aljeboree 2015; Aljeboree 2016) .The equilibrium sorption capacity was minimum at pH 2 (12.5mg/g) and increased up to pH6, reached maximum (68.3 mg/g) over the initial pH show in Fig. 7. The absence of sorption at neutral pH(6) can be explained by the fact that at this acidic pH, H+ may compete with drug ions for the adsorption sites of adsorbent, thereby inhibiting the adsorption of drug. after neutral pH(6) adsorption showed insignificant variation, thereby supporting that no ion exchange mechanism is involved. The physical forces like van der Waal's, hydrogen bonding, dipole–dipole interactions may contribute to this higher adsorption (Thitame and Shukla 2016).

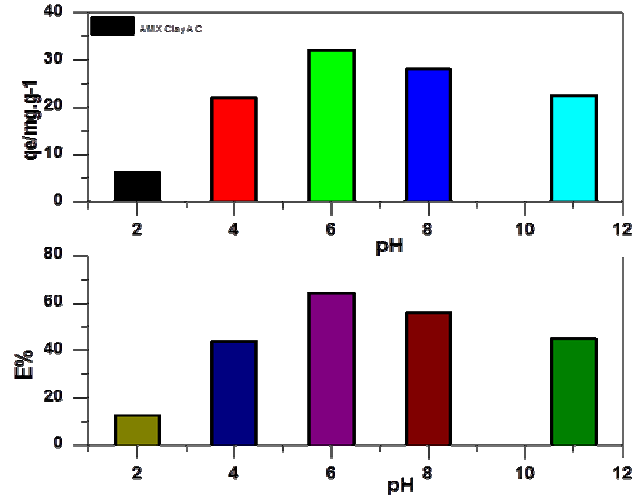

Fig. 7 : Effect of solution pH on the percent removal and amount of adsorbed AMX drug onto (CDCN) initial concentration = 50 mg/L, Temp. = 25°C, contact time 1 h, and mass of adsorbent 0.1 g/L).

Adsorption Isotherms

The adsorption data were analyzed using adsorption isotherm models, Langmuir and Freundlich. The Langmuir model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The expression of the Langmuir model is given by the following equation (Choy, Porter *et al*., 2000):

$$Q_e = \frac{QmK_LC_e}{1+K_LC_e} \quad ....(3)$$

Where Q_e (mg/g) and C_e(mg/L) are the amounts of adsorbed drug per unit mass of sorbent and drug concentration in solution at equilibrium, respectively. Q_m is the maximum amount of the adsorbed drug per unit mass of sorbent to form a complete monolayer on the surface bound at high C_e (mg/g), and K_L (L/mg) is a Langmuir constant related to the affinity of the binding sites on the adsorbent surface. (Thitame and Shukla 2016) :

The Freundlich model assumes heterogeneous adsorption due to the diversity of active sites on the surface. The Freundlich equation is expressed as (Freundlich, 1939):

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

While K_f (L/mg) is the Freundlich constant, and 1/*n* is the heterogeneity factor.

K_f can be defined as the adsorption or distribution coefficient and represents the quantity of drug adsorbed onto adsorbent for unit equilibrium concentration. 1/n is the heterogeneity factor. A value for 1/n below one indicates a normal Freundlich isotherm while 1/n above one is an indicative of cooperative adsorption.

A plot of qe-versus Ce is shown in Fig 8, 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= 0.9932). 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=0.9679). Results are shown in (Fig. 6), the calculated parameters of two models are illustrated in Table 1.

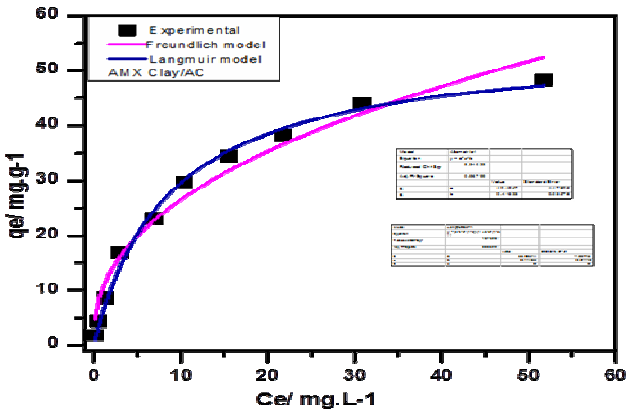

Fig. 8 : Different adsorption isotherm models nonlinear fit for adsorption of AMX drug on (CDCN) ,initial concentration=50 mg/L, Temp.=25°C, contact time 1 h, and mass of adsorbent 0.1 g/L).

Table 1: Langmuir and Freundlich, model isotherms parameters for AMX drug adsorbed on the surface of (CDCN) at 25 ºC.

Isotherm models	Parameters	AMX drug
Langmuir	qm ($mg.g^{-1}$)	1.8017± 55.2867
	K_L($L.mg^{-1}$)	0.0111±0.1145
	R^2	0.9932
Freundlich	K_F	1.778± 10.1547
	1/n	0.0358± 0.4162
	R^2	0.9679

Conclusion

The results of different experiments showed that a (CDCN) that considered a friendly of the environment have ability to adsorb amoxicillin drug from aqueous solution. The sorption process dependent of the pH and was found the best result at pH 6 and the adsorption process has nearly reached equilibrium in 60 min. The experimental data are fitted well to Langmuir isotherm model, and the maximum adsorptive quantity of amoxicillin was 48.25 mg/g according to Langmuir model.

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