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Research Article

Adsorption of amoxicillin onto Activated Carbon from aqueous solution

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Abstract

In this study the uptake of Amoxicillin(AMX) at different parameters such as (initial concentration of amoxicillin (50-350ppm), contact time and different dosage of activated carbon (0.5-1gm).Batch adsorption study was adopted to calculate the experimental adsorption isotherm information for several initial concentrations of AMX (50 - 350 mg/l). The equilibrium information were analyzed using Langmuir, Freundlich and Brunauer–Emmett–Teller (BET) models. The results displayed that the experimental data were good fitted with Freundlich isotherm. Pseudo- first order, pseudo- second order, as well as intraparticle diffusion models were utilized to analyze experimental kinetics data with high correlation coefficient for pseudo- first - order model.

Keywords: *Adsorption, Activated carbon , Amoxicillin,Batch adsorption, uptake*

1. Introduction

Adsorption has become a common and sometimes used technique for the removal of pollutants. The more common adsorbents, activated carbon continues to be the foremost wide used for the purification of water with low pollutant concentration (Mestre,*et.al,*2009). Adsorption normally refers to while atoms move from a bulk phase onto the surface of either a solid or a liquid. An example of this is often once impurities are filtered from liquids or gases. This project based on liquid phase adsorption. Adsorption in the liquid phase is influenced by several factors. Simple factors like pH, type of adsorbent, solubility of adsorbent within the solvent, and temperature all have an influence on liquid phase adsorption (Rogue-Mahbe, 2007). Adsorption is a method with three steps. The primary of those steps is for the contaminant to be transferred from the bulk phase to the outer surface of the sorbent. Within the second step, the contaminant molecule diffuses from the smaller of the areas of the outer surface into the areas inside every adsorbent. This includes the macropores, transitional pores, and micropores. The last step is when the contaminant molecule is adsorbed into the surface of the pore structure inside the adsorbent (Sarah,*et.al,*2013) .The conventional chemical processes for removing pollutants from wastewater include many processes such as chemical precipitation, adsorption, ion exchange, and electrochemical process. Chemical precipitation is one of the most widely used for pollutants removal from inorganic effluent in industry due to its simple operation. The mechanism of this process is based on to produce insoluble pollutant precipitation by reacting dissolved pollutants in the solution and precipitant. In the precipitation process very fine particles are generated and chemical precipitants, coagulants, and flocculation processes are used to increase their particle size to remove them as sludge. Removal percentage of pollutant ions in the solution may be improved to optimum by changing major parameters such as pH, temperature initial concentration, charge of the ions etc.

The most commonly used precipitation technique is hydroxide treatment due to its relative simplicity, low cost of precipitant (lime), and ease of automatic pH control (Fu and wang,2011),(Jung,2001).Ion exchange can attract soluble ions from the liquid phase to the solid phase, which is the most widely used method in water treatment industry. As a cost-effective method, ion exchange process normally involves low-cost materials and convenient operations, and it has been proved to be very effective for removing pollutants from aqueous solutions, particular for treating water with low concentration of pollutants. In this process cations or anions containing special ion exchanger is used to remove pollutant ions in the solution. Commonly used ion exchangers are synthetic organic ion exchange resins. It can be used only low concentrated pollutant solution and this method is highly sensitive with the pH of the aqueous phase. Ion exchange resins are water-insoluble solid substances which can absorb positively or negatively charged ions from an electrolyte solution and release other ions

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with the same charges into the solution in an equivalent amount (Dizge and Barlas,2009), (Hamdaui,2009). Electrolysis: Electrolytic recovery is one technology used to remove pollutants from wastewater streams. This process uses electricity to pass a current through an aqueous pollutant-bearing solution containing a cathode plate and an insoluble anode. Electricity can be generated by movements of electrons from one element to another. Electrochemical process to treat wastewater containing pollutants is to precipitate the pollutants in a weak acidic or neutralized catholyte as hydroxides. Electrochemical treatments of wastewater involve electro-deposition, electro-coagulation, electro-flotation and electro-oxidation(Shim,*et.al,*,2014).

2. Mathematical Models

2.1. Adsorption Isotherm

The adsorption isotherm indicates the sorption molecules extend between the liquid /solid phase the adsorption operation reaches an equilibrium case. The analysis of the isotherm information by fitting them to several isotherm models could be major step to detection the suitable model that may be used for design objectives . Most adsorption isotherms is also classified into six kinds, that are considerably indicated to as the Langmuir , Freundlich , Temkin, Sips, Brunauer-Emmett Teller and Dubinin-Radushkevich classification. In all cases the adsorbed quantity of adsorbate is progressively increases as its concentration is raise , becoming at some point equivalent to a monolayer, then again will increase to a multilayer, that finally combine into a condensed phase(Masel,1996).

2.1.1. Langmuir Isotherm

Langmuir assumes monolayer adsorption onto a surface consist of a finite number of adsorption sites of uniform strategies of adsorption with immigration of adsorbate within the plane of surface. The Langmuir isotherm equation is performed by the following equation (Cheremisinoff and Morrres,1987).

$$q_e = \frac{q_m K_l C_e}{1+K_l C_e} \quad (1)$$

Where Ce (mg/l) is the equilibrium concentration of solute, qe (mg/g) is the uptake at equilibrium, K_l (l/mg) is the constant related to free energy of adsorption, and q_m (mg/g) is the maximum uptake at monolayer coverage. The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant known as separation agent or equilibrium parameter *R*L, determined as

$$R_L \frac{1}{1+K_l C_e} \quad (2)$$

The separation agent (R_L), an important parameter of the Langmuir isotherm, may be used to reality the adsorption as unfavorable ($R_L > 1$), and linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$)

2.1.2. Fruendlich Isotherm

The Freundlich isotherm is an empirical equation that may be used for heterogeneous system with interaction between the molecules adsorbed (Freundlich,1906). Freundlich isotherm assumes heterogeneous surface energies, within which the energy term in Langmuir equation different as a function of the surface concealment. The Freundlich model is given by the following equation.

$$q_e = K_f C_e^{1/n} \quad (3)$$

where q_e is the uptake at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l), K_f is the Freundlich isotherm constant associated with adsorption capacity(1/mg)$(1/mg)^{1/n}$). n is the Freundlich isotherm constant relating to adsorption intensity .1/n ranging between 0 and 1 may be a measurement of adsorption strength or surface heterogeneity, becoming further heterogeneous as its value gets closer to zero. A value for 1/n below one indicates a normal Langmuir model while 1/n above one is indicative of cooperative adsorption (Cheremisinoff and Morrres,1987).

2.1.3. Brunauer–Emmett–Teller model (BET)

The BET model assumes that layers of molecules are adsorbed on top of previously adsorbed molecules. Each layer adsorbs according to the Langmuir adsorption model. The BET equation has the following formula for adsorption from a liquid solution:

$$q_e = \frac{q_m K_B C_e}{(C_o - C_e)\left[1+(K_B-1)\frac{C_e}{C_o}\right]} \quad (4)$$

Where *qm* is the maximum adsorption capacity (mg/g); *Co* initial concentration of adsorbate at saturation of all layers; and *KB* constant related to energy of interaction between adsorbent and adsorbate (alaa,2016).

2.2. Adsorption Kietics

Much adsorption kinetic models have been approved to characterize the manner of batch biosorption processes in various experimental conditions. Kinetics of adsorption is one of the major characteristics defining the efficiency of adsorption.

2.2.1 Pseudo first order model

The Lagergren rate equation can have been the first rate equation for the sorption in liquid /solid systems depending on solid efficiency. The Lagergren rate equation is the most excessively utilized rate equation for sorption of a solute from a liquid solution (Ho and Mckay,2000).

$$\frac{d_q}{d_t} = K_1(q_e - q_t) \quad (5)$$

Integrating for the initial and final conditions (t = 0 to t = t) and (qt = 0 to qt = qt), equation (5) may be rearranged for linearized data plotting as shown by equation (6):

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (6)$$

Where: q_e and q_t are uptake at Equilibrium and at time t, respectively (mg/g), K_1 is the pseudo first order rate constant (1/min).

2.2.2 Pseudo-Second Order Model

The pseudo second-order kinetic model may be represented as follows:

$$\frac{d_{qt}}{d_t} = K_2(q_t - q_e)^2 \quad (7)$$

Integration Eq. (7) for the boundary condition t=0 to t=t and q=0 to q=qt and rearranged in a linear form gives Eq. (8) (Qiu *et al.*, 2009).

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

Where K_2 (g/mg.min) the equilibrium rate constant of pseudo second-order model. A plot of t/q_t versus t gives a liner relationship from that q_e and K_2 were established from the slope and intercept of the plot, respectively. This equation has been swimmingly utilized to the adsorption of organic substances, metal ions, dyes, herbicides and oils (Qiu,*et.al*,,2009).

2.2.3 Intra-particle diffusion model

The possibility of intra-particle diffusion of adsorbate onto the adsorbent by using the intra-particle diffusion model Eq. (9)

$$q_t = K_3 t^{1/2} + C \quad (9)$$

q_t the amount of AMX adsorbed (mg/g) at time t, C (mg/g) is the is the boundary layer thickness and Kp is the rate constant of intra-particle diffusion model (mg/g.$s^{1/2}$) (Abood,2012).

3. Experimental Work and Materials

3.1. Adsorbate

Amoxicillin AMX ($C_{16}H_{19}N_3C_5S$) was utilized as an adsorbate with molecular weight of 365.4 g/mol. A stock solution of400 mg/L was prepared by dissolving amount of AMX in distilled water (As it is taken from the Arab Company for the manufacture of antibiotics and accessories form (Akai)) and then diluted to the desired concentrations

3.2. Adsorbent

Activated carbon was washed with distilled water to eliminate dust, dried by placing at 80°C for 24h and cut to a very small size. Then it was sieved into a uniform size of (300-1000)µm.

3.3. Batch Experiments

3.3.1 Contact time experiment

The influence of contact time on uptake of AMX can be procedure via producing adsorbent–adsorbate solution with constant adsorbent dose of 0.7 g of solution with initial AMX concentration of 150mg/L for various time periods and shaken at 200 rpm samples were taken after 30 min until equilibrium is reached, then samples are analyzed to measure the AMX concentration which adsorbed versus time.

3.3.2.Adsorbent dosage experiment

A weight of an adsorbent has an most influence of AMX uptake. Various weights of (0.5,0.7 and 1) g added to 100 mL of AMX solution of 150 mg/L shaken at 200 rpm to calculate the AMX uptake(q_e):

3.3.3 Initial AMX concentration experiment

The uptake of AMX is much based on the initial amount of AMX concentration . To study the influence of initial concentration, 100 mL of various concentrations (50,150 and 350) mg/L and 0.5 g of adsorbent and shaken at 200 rpm samples were analyzed to calculate the uptake of AMX q_e for several concentrations.

4. Results and Discussion

4.1. Equilibrium Experiments

4. 1.1 Effect of contact time

The influence of contact time on the AMX uptake of prepared activated carbon at 150 ppm initial concentration of AMX is shown in figure1.

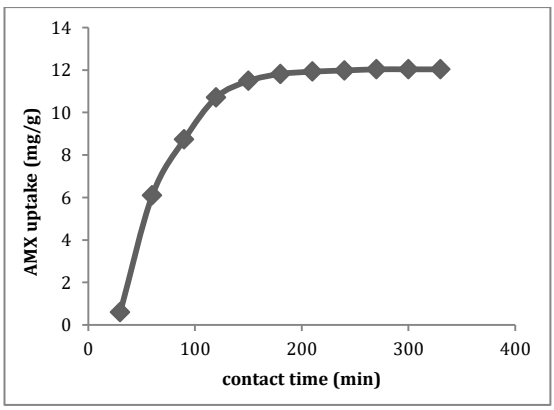


Fig.1 Effect of contact time on AMX uptake at C_o 150 mg/L, dosage 0.7 g

The uptake of AMX will increase when the contact time increased and reach to equilibrium after 270 minutes. The maximum uptake of AMX is 12.033 mg/g. After equilibrium time, adsorption is will be nearly constant and the AMX uptake does not display any considerable results. This is fundamentally due to in the initial time of adsorption, empty surface sites are available, once equilibrium is attained; the remaining vacant sites are difficult to be occupied (Adamu,2008),(Bharathi and Rames,2013).

4.1.2 Effect of initial concentration

The initial AMX concentration equipped an important driving force to overcome resistant encountered when molecules are transferred between liquid and solid phases (Moussavi and Khosravi, 2011). Figure2 show the influence of initial AMX concentration on the adsorption operation. From this figure the AMX uptake increases with initial AMX concentration increasing, under the slimier conditions when concentration in the solution was higher, a high number of ions, resulting in a much enough adsorption, surrounded the active sites of adsorbent. Therefore, the values of q_e increased with an increase in initial concentrations. furthermore this may be because to the high driving force for mass transfer at high initial AMX concentration((Bharathi and Rames,2013),(Yagub,*et.al,*,2014),(Aksakal and Ucan,2010).

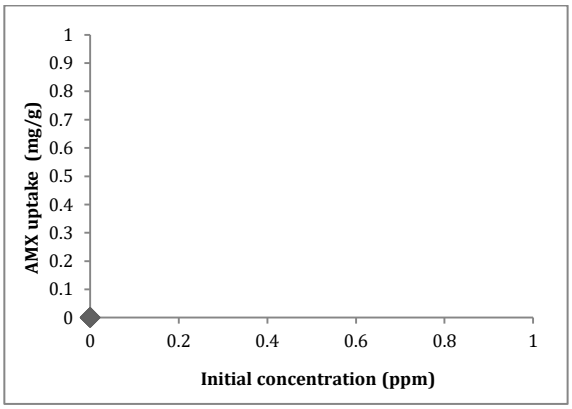


Fig.2 Effect of initial concentration on AMX uptake (dosage0.5 g)

4.1.3 Effect of adsorbent dose

The influence of adsorbent dosage provides a conception for the ability of AMX to be adsorbed with the smallest quantity of adsorbent, to knowledge the ability of AMX removal from an economic point of view (Yagub,*et.al,*,2014). Figure 3 showed that the adsorption uptake is decreases with increasing adsorbent quantity at constant AMX concentration and volume of AMX solution and that can be referred to saturation of adsorption sites on adsorbent surface because of particulate interaction such as aggregation. Aggregation would lead to a lessening in total surface area of the adsorbent and a boost in diffusion path length, or might be because of that the adsorptive capacity of the adsorbent was available and was not completely employed at higher adsorbent dosage in compare to lower adsorbent dosage, this is probably due to the equilibrium concentration difference, where there was a lower driving force for adsorption at higher adsorbent dosage occurred (Su,*et.al,*,2014), (Pirbazari,*et.al,*,2014).

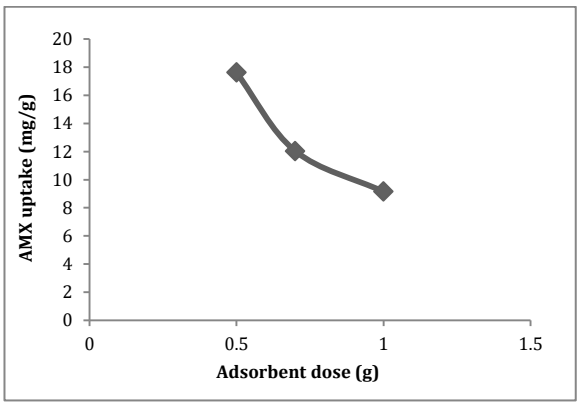


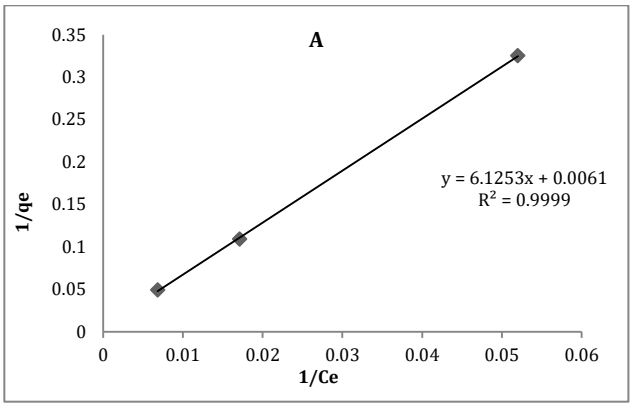
Fig3 Effect of adsorbent dosage on AMX uptake at C_o = 150 ppm

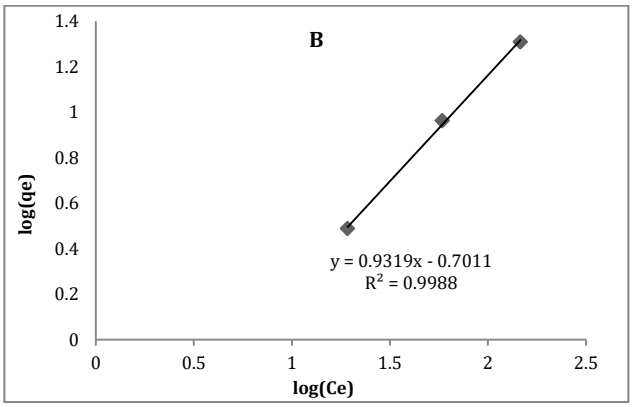
4.2 Isotherm Study

The adsorption isotherm represent the interaction between the adsorbate and the adsorbent. Adsorption equilibrium is happens when an adsorbate has be contacted with the adsorbent for sufficient time, and the adsorbate concentration in the solid phase is at a balance with its concentration in the liquid phase (Foo and Hameed,2012d). Studying of such isotherms is main step so as to find a suitable model that carefully represents the results and would be used in design purposes (Mahmoud,2014). The experimental equilibrium data for AMX adsorption on activated carbon which fitted to the Langmuir, Freundlich, and BET isotherms, Equations (1),(3),(4) are represented in Figures(4) .The results are summarized in Table 1.

Table 1 Isotherm Parameters for AMX uptake on Activated

Isotherms	Parameters	Values
Langmuir	q_m(mg/g) K_L(1/mg) R_L R^2	163.93 0.00099 0.9333 0.9999
Freundlich	K_f n R^2	0.199 1.073 0.9988
Brunauer Emmett Teller (BET)	q_m(mg/g) K_B R^2	-.0477 -1.384 0.5733





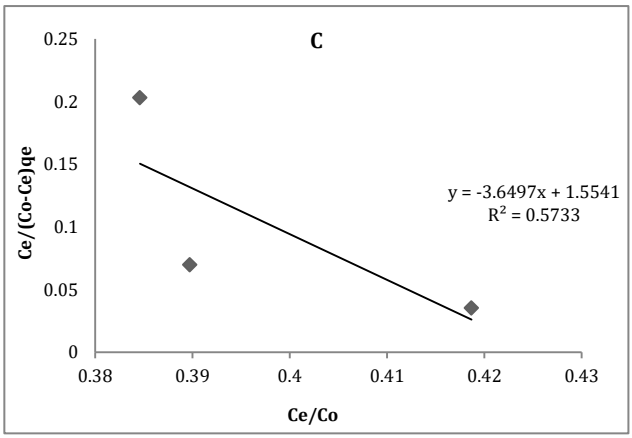


Fig.4 Isotherms adsorption of AMX where (A:Langmuir, B:Freundlich and C:BET)

Show that Langmuir isotherm has the highest R^2 value as compared to that of both Freundlich and BET isotherms. Figure 5 show the comparison between the uptake of AMX from experimental data and the uptake of AMX calculated from Langmuir, Freundlich and BET isotherms models.

From figure 5 indicates that the homogeneous nature of the surfaces of adsorbents (activated carbon have homogenous distribution active sites) and describes the data of the monolayer of the AMX molecule over the adsorbent surface indicates the chemical nature of the adsorption reaction (Chemisorption interaction) (Mohan,*et.al,*,2002).

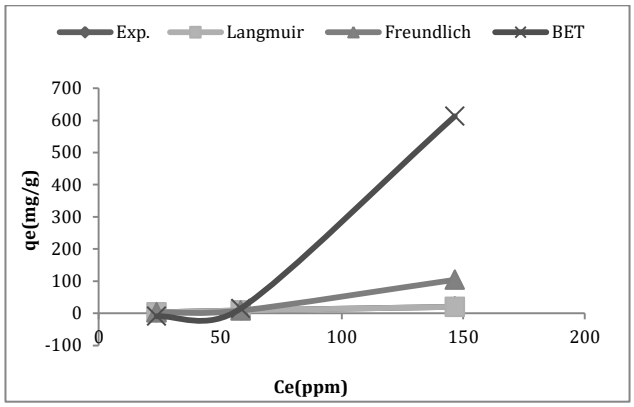


Fig.5 Comparison between experimental data and theoretical data

4.3 Kinetic Study

The study of adsorption kinetics shows how the solute uptake capacity and clearly this capacity control the existence time of the adsorbate at the solution interface. This capacity is very important when designing the adsorption system and this capacity will be calculated from kinetic study (Yagub,*et.al,*,2014). Figures 6, 7 and 8 shows the enforcement of pseudo first, second order and intraparticle diffusion models by applying Equations. (6), (8) and (9).

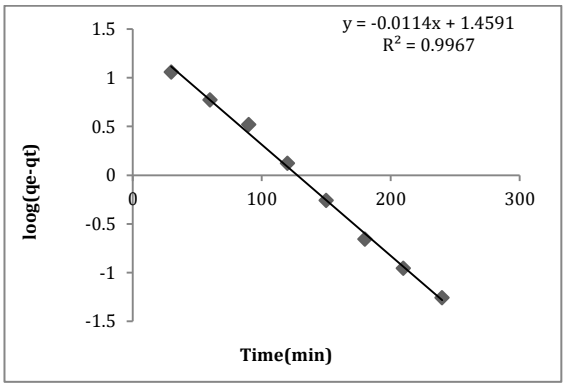


Fig.6 Pseudo-first order kinetic for AMX adsorption on AC [initial concentration=150ppm, dose= 0.7 g]

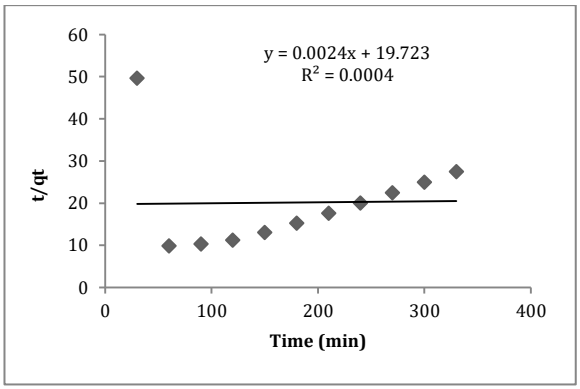


Fig.7 Pseudo-second order kinetic for AMX adsorption on AC [initial concentration =150ppm, dose = 0.7 g]

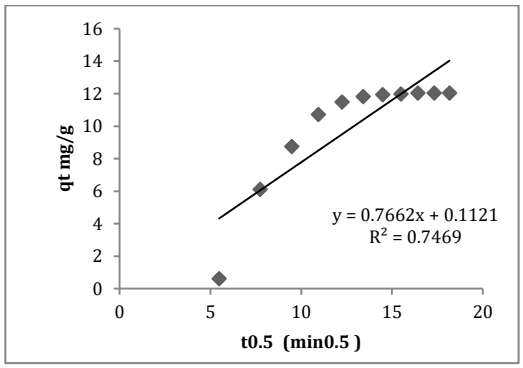


Fig.8 Intraparticle diffusion plot for AMX adsorption [initial concentration=150ppm,dose = 0.7g]

Table 2 Kinetic parameters for AMX adsorption on AC

Models	Parameters	Values
Pseudo first order	q_e, cal (mg/g)	28.78
	K_1(1/min)	0.02625
	R^2	0.9967
	q_e, cal (mg/g)	316.67
Pseudo-second order	K_2 (g/mg.min)	0.00012168
	R^2	0.0004
Interpartical diffusion	q_e, cal (mg/g)	0.1121
	K_3 (mg/g.min$^{1/2}$)	0.7662
	R^2	0.7469

The pseudo- first order equation is of high R^2 value as compared to the pseudo- second order equation, as shown in Table2. The results of the table show that the adsorption kinetics data are better represented by pseudo- first order model and the calculated q_e value. This meaning that the first -order kinetics is higher compared to other models for AMX adsorption on AC.

Conclusion

In order to the results of this study, the conclusions are

1. In batch experiments: the experimental data of AMX uptake on activated carbon were fitted to three models (Langmuir , Freundlich and Brunauer–Emmett–Teller models). The results of this fitted shows that the experimental data was fitted to Langmuir model.
2. In experiment of the effect of contact time the experimental data are fitted to three models which pseudo first order, pseudo second order and Interpartical diffusion. The results of this fitted indicate that the experimental data was fitted to pseudo first order.

References

Mestre, A. S.; Pires, J.; Nogueira, J. M. F.; Parra, J. B.; Carvalho, A. P.; Ania, C.O.(2009), Waste-derived activated carbons for removal of ibuprofen from solution: Role of surface chemistry and pore structure,*Bioresource Technology*, 100(5), 1720-1726

Rogue-Malherbe, R. M. (2007), Adsorption from liquid solution *Adsorption and diffusion in nonporous materials*, 243-244-258. CRC Press.

Sarah Connors, CHE Renee Lanza, EVE Alexander Sirocki, EVE (2013), Removal of Ibuprofen from Drinking Water using Adsorption, *Major Qualifying Project completed in partial fulfillment Of the Bachelor of Science Degree at Worcester Polytechnic Institute, Worcester, MA*

Fu, F. and Q. Wang, 2011,Removal of heavy metal ions from wastewaters: a review, *Journal of Environmental Management,*. 92(3): p. 407-418.

Ku, Y. and I.-L. Jung, 2001Photo catalytic reduction of Cr (VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide *Water Research,*. 35(1): p. 135-142.

Dizge, N., B. Keskinler, and H. Barlas, 2009 Sorption of Ni (II) ions from aqueous solution by Lewatit cation-exchange resin. *Journal of hazardous materials,*. 167(1): p. 915-926.

Hamdaoui, O., 2009 Removal of copper (II) from aqueous phase by Purolite C100-MB cation exchange resin in fixed bed columns: Modeling. *Journal of hazardous materials,*. 161(2): p. 737-746.

Shim, H.Y., 2014 Application of Electro coagulation and Electrolysis on the Precipitation of Heavy Metals and Particulate Solids in Wash water from the Soil Washing, *Journal of Agricultural Chemistry and Environment,*. 3(04): p. 130.

Masel, R.I. (1996). Principles of Adsorption and Reaction on Solid Surfaces.*3rd ed. John Wiley & Sons, New York*

Cheremisinoff, P.N. and Morresi, A.C. (1987) Carbon adsorption application. In P.N.Cheremisinoff and F. Ellerbusch ,Carbon Adsorption, *Handbook. Michigan: Ann Arbor Science.*

Freundlich, H.M.F., Z. 1906, Uber die adsorption in losungen,57, 385–470.

Alaa Hussein Taha,2016 Removal of textile dyes by using wheat straw as adsorbent, A Msc. Thesis, Al-Nahrain University

Ho Y., Ng J. and McKay G., (2000), Kinetics of pollutant sorption by biosorbents: review, *Separation & Purification Reviews*, 29, 189-232.

Qiu, H., Lv, L., Pan, B., Zhang, Q., Zhang, W. and Zhang, X. (2009). Critical review in adsorption kinetic models, *Journal of Zhejiang University Science*, 10(5), 716-724.

Abood W. M., (2012), Removal of three textile reactive dyes (Blue, Red and Yellow) by Activated carbon and Low-Cost Adsorbents, Ph.D. Thesis, University of Baghdad.

Adamu A., (2008), Adsorptive removal of reactive azo dyes using industrial residue, M.Sc Thesis, Addis Ababa University.

Bharathi K. and Ramesh S., (2013), Removal of dyes using agricultural waste as low-cost adsorbents: a review, *Applied Water Science*, 3, 773-790.

Yagub M. T., Sen T. K., Afroze S. and Ang H. M., (2014), Dye and its removal from aqueous solution by adsorption: a review, *Advances in colloid and interface science*, 209, 172-184.

Aksakal O. and Ucun H., (2010), Equilibrium, kinetic and thermodynamic studies of the biosorption of textile dye (Reactive Red 195) onto Pinussylvestris L, *Journal of Hazardous Materials*, 181, 666-672.

Su Y., Jiao Y., Dou C. and Han R., (2014), Biosorption of methyl orange from aqueous solutions using cationic surfactant-modified wheat straw in batch mode, *Desalination and Water Treatment*, 52, 6145-6155.

Pirbazari A. E., Saberikhah E. and Kozani S. H., (2014), Fe_3O_4–wheat straw: preparation, characterization and its application for methylene blue adsorption, *Water Resources and Industry*, 7, 23-37.

Foo, K.Y. and Hameed, B.H. (2012d), Mesopores activated carbon from wood sawdust by K2CO3 activation using microwave heating *Bioresource Technology,*111 ,425–432

Mahmoud M. S., (2014), Decolonization of certain reactive dye from aqueous solution using Baker's Yeast (Saccharomyces cerevisiae) strain, *Housing and Building National Research Center.*

Mohan S. V., Rao N. C. and Karthikeyan J., (2002), Adsorptive removal of direct azo dye from aqueous phase onto coal based sorbents: a kinetic and mechanistic study, *Journal of hazardous materials,* 90, 189-204.