International Journal of Current Engineering and Technology
E-ISSN 2277 – 4106, P-ISSN 2347 – 5161

Research Article

Adsorption of Salicylic and Sulfosalicylic Acid onto Powdered Activated Carbon prepared from Rice and Coffee Husks

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Accepted 05 May 2015, Available online 12 May 2015, **Vol.5, No.3 (June 2015)**

Abstract

Activated carbons prepared by chemical activation of rice and coffee husks with phosphoric acid were used to study the adsorption of salicylic and sulfosalicylic acids. The characterization of the prepared activated carbons showed that the pH at zero charge was between 2.3 and 3.45; the bulk density was around 0.800 g/cm^3 and the iodine number was between 476 and 590 mg/g. The adsorption process took place in two stages, and the adsorbents had a good affinity for the two acids. The adsorption capacity was found to increase with increasing molar mass of the adsorbates, and the best pH for adsorption of 2 was below the pH of zero charge. The kinetic and equilibrium examination of the process showed the adsorption to be chemical in nature, exothermic and occurred only over a monolayer.

Keywords: *adsorption, activated carbon, phenolic compounds, rice and coffee husks.*

Introduction

Phenolic compounds disposed into the environment have been a major cause for concern as they are bactericide molecules that destroy the bacteria in the environment. These are effluents generated by agrochemical and pharmaceutical industries. The increasing demand for food and medical products makes the deposition of phenolic products into the environment reach an alarming amounts. It thus appears necessary to limit the use of potentially dangerous chemicals and to minimize their disposal into the natural environment. This can be achieved by treating the effluents generated by both domestic and industrial activities (Morlay, 2006).

Since the 1980s, effluents from pharmaceutical industries have been subjected to analyses (Chafai, *et al,* 2013). These analyses have shown that salicylic acid is present in waste streams from these industries. Their concentrations greatly exceed the limit amount of 37 mg/L which exhibits toxic effect. This is much greater than the highest concentrations of salicylic acids due to natural phenomena which is only 60 µg/L (Hao, *et al*, 2000). The elimination of salicylic and sulfosalicylic acids from acutely contaminated areas by oxidation has already been the subject of several studies (Djouder, *et al*, 2012).

Activated carbon prepared by chemical activation of local biomass has been used for the adsorption of various organic compounds and heavy metals from the environment (Devi, *et al*, 2012; Gueye, *et al*, 2014). The advantage of chemical activation is that pyrolysis is achieved at low temperature, thereby greatly reducing the cost of the activated carbon. Activated carbon of good quality, with a very significant porous structure and a large specific surface area was prepared from vegetable biomass materials using activating agents like phosphoric acid, zinc chloride, sodium hydroxyde and potassium hydroxyde.

During the last few years, agricultural products, which are abundantly available have also constituted precursors for the production of activated carbons. For example, activated carbon has been produced from various carbonaceous materials resulting from agriculture such as ground nut shell (Gueye, *et al*, 2014), maize cob (Dina *et al*, 2012), (El-Hendawy, *et al*, 2001), apple husks (Suàrez-Garcia, *et al*, 2001), date pits (Girgis and El-Hendawy, 2002), olive stones (Rodriguez, *et al*, 2008), (Bohli, *et al*, 2013), waste tea (Yagmur, *et al*, 2008), bagasse (Valix, *et al*, 2004), and coconut shells (Laine, *et al*, 1989).

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This work presents a double objective: the first is the valorization of rice and coffee husks for the preparation of the activated carbon by chemical activation, and the second is to use these activated carbons for the adsorption of the salicylic and sulfosalicylic acids from aqueous solution. The study will involve the determination of parameters that are likely to affect the quantity of organic compounds adsorbed such as, the time of contact, initial pH of the solution, mass of the adsorbent and initial concentration of the adsorbates.

Materials and method

Preparation and Characterization of Activated Carbons

Rice and coffee husks were used as raw materials to produce activated carbons by chemical activation with phosphoric acid followed by carbonization. The rice husk was obtained from the local rice processing mill in Ndop Subdivision in the North West Region, while the coffee husk was obtained from Santchou Subdivision in the West Region, both in Cameroon.

Each raw material was washed with tap water followed by distilled water and sun dried for 72 hours before activation. To obtain an activated carbon, 20 g of dried raw material was mixed with 35 g of 1 M solution of phosphoric acid and allowed for 30 minutes before being dried in an oven set at 105°C. An ISUNU electric furnace with automatic regulation and having a temperature programmer coupled to the furnace regulation was used.

The activated carbon (CAH1) was obtained by carbonizing the activated rice husks through heating at 500°C for one hour of 5°C/min. CAH2 was obtained by carbonizing rice husks at 450°C at a heating rate of 5°C/min, while CAMH was obtained by carbonizing a mixture 12 g rice husk and 8 g coffee husk at 500°C. The various activated carbons were dried in an oven set at 105°C for 24 hours before being ground and sieved to obtain particles of sizes lower than 100 μm.
The activated carbons were characterized to have the pH at zero charge pH_{PCZ}, the bulk density, moisture content, pH and iodine number.

Adsorption

Adsorption experiments were carried out by mechanical agitation at room temperature. For each run, 20 mL of salicylic acid or sulfosalicylic acid, of known initial concentration (50-110 mg/L) was treated with a known weight of activated carbon at pH = 2. After agitation for a given time, the solution was filtered and the filtrate subsequently analyzed for concentration by UV/Vis spectrophotometer, Jenway model 6715. The spectrophotometer was set at the wavelength 296.5 nm for salicylic acid, and at 294.5 nm for sulfosalicylic acid. Similar measurements were carried out by varying adsorbent doses, pH and initial concentrations. The percentage removal (%R) and the amount (Q_e) adsorbed were calculated using the following expressions:

$$\%R = 100\frac{C_0 - C_t}{C_0} \tag{1}$$

$$Q_e = \frac{C_0 - C_e}{m}V \tag{2}$$

C_o is the initial concentration, C_e is the equilibrium concentration, C_t is the concentration of solution at the time t, V is the volume of the solution, and m is the mass of the adsorbent.

Effect of contact time

To determine the effect of agitation time on the removal process, 20 mL of solution of concentration 70 mg/L was agitated with 50 mg of activated carbon for salicylic acid adsorption, and 100 mg for sulfosalicylic acid for different time intervals. After each time interval, the solution was rapidly filtered and the residual acid concentration determined by spectrophotometer. The percentage removal (%R) of acid was calculated by using Equation (1).

Effect of amount of adsorbent

In this set of experiments, different masses of the adsorbents ranging from 25 mg to 200 mg were treated with 20 mL acid solution of initial concentration 70 mg/L; the agitation times used were the optimum times obtained from the effect of contact time experiments.

Effect of initial pH

To determine the effect of pH, the adsorption of salicylic and sulfosalicylic acids by the activated carbons were investigated over a pH range of 2 to 7 at ambient temperature. Each run consisted of 20 mL solution of initial solute concentration of 70 mg/L and an adsorbent mass of 100 mg for sulfosalicylic and 50 mg for salicylic acid adsorption. The initial pH of the solution was adjusted by adding 0.001 M H_2SO_4 or 0.001 M NaOH solutions.

Kinetics of adsorption studies

The kinetics experiments were conducted using a series of 20 mL solutions containing known masses of adsorbents and known concentrations of adsorbates. The solutions were vigorously agitated for increasing time intervals. At the end of each time, the solution was analyzed to determine the residual concentration of adsorbate. A number of kinetic models were used to fit the experimental data. These are:

The pseudo-first order model

The pseudo-first order equation is generally expressed as (Anagho, *et al*, 2013):

$$\frac{dQ}{dt} = K_1(Q_e - Q_t) \quad (3)$$

Where Q_e and Q_t are the adsorption capacity at equilibrium and at time t, respectively (in mg/g) and K_1 is the rate constant for the pseudo-first order adsorption (L/min). After integration and applying boundary conditions that at t = 0, Q_t = 0; and at t = t, Q_t =Q_t, the integrated form of equation (3) becomes:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (4)$$

The pseudo-second order model

The pseudo-second order chemisorption kinetic equation (Ho and Mckay) (Ho and McKay, 1999) is expressed as equation 5:

$$\frac{dQ_t}{dt} = K_2(Q_e\text{-}Q_t)^2 \quad (5)$$

Where K_2 is the rate constant for the pseudo-second order adsorption (g/mg.min). Using the boundary conditions that at t = 0, Q_t = 0; and at t = t, $Q_t = Q_t$, the integrated and rearranged form of equation (5) is:

$$\frac{t}{Q_t} = \frac{1}{K_2 {Q_e}^2} + \frac{t}{Q_e} \quad (6)$$

The Elovich kinetic equation

The Elovich equation is generally expressed as (Ndi, *et al*, 2014):

$$\frac{dQ_t}{dt} = \alpha e^{-\beta Q_t} \quad (7)$$

Where α is the initial adsorption rate (mg/g.min), and β is the desorption rate constant (mg/g.min).

The integrated and simplified equation (assuming that $\alpha\beta t >> 1$) is:

$$Q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad (8)$$

Intraparticle diffusion model

Weber-Morris found that in many adsorption cases, solute uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time t (Qiu, *et al*, 2009). For example, the rate of adsorption can be expressed as (Igwé, *et al*, 2008):

$$Q_t = X_i + K^1 t^{0.5} \quad (9)$$

Where X_i is the boundary layer diffusion effects, and it depicts the boundary layer thickness, while K_{id} (mg/g.min) is the initial rate of adsorption, and it is controlled by intra-particle diffusivity.

Batch equilibrium experiments

For each run, the adsorbent was mixed with 20 mL solution of adsorbate at different initial concentrations from 50-110 mg/L. The suspension was stirred for 100 minutes for salicylic acid and 120 minutes for sulfosalicylic acid. The amount of each acid adsorbed at equilibrium, Q_e (mg/g) was calculated using equation (2). Equilibrium data were then fitted by using the isotherms of Langmuir, Freundlich and Temkin.

The Langmuir Isotherm

The Langmuir adsorption isotherm is often used to express the equilibrium of the adsorption of solutes from solutions. It is expressed as (Ketcha, *et al*, 2011):

$$Q_e = Q_m \frac{K_L C_e}{1 + K_L C_e} \quad (10)$$

Where, Q_e is the adsorption capacity at the equilibrium solute concentration, in mg of adsorbate per g of adsorbent; C_e is the equilibrium concentration of adsorbate in solution (mg/L), while Q_m is the maximum adsorption capacity corresponding to complete monolayer coverage of the adsorbent surface, expressed in mg of solute adsorbed per g of adsorbent. K_L is the Langmuir constant, expressed in L of adsorbate per mg of adsorbent, and it is related to the energy of adsorption. Equation (10) can be rearranged to the linear form:

$$\frac{1}{Q_e} = \frac{1}{Q_m K C_e} + \frac{1}{Q_m} \quad (11)$$

The factor of separation of Langmuir, R_L, which is an essential factor characteristic of this isotherm is calculated by using the relation (Maarof, *et al*, 2004):

$$R_L = \frac{1}{1 + K C_0} \quad (12)$$

Where C_0 is the higher initial concentration of adsorbate, while K_L and Q_m are the Langmuir constant and the maximum adsorption capacity respectively.

The Freundlich Isotherm

The Freundlich isotherm is based on adsorption on a heterogeneous surface, and it is expressed as (Hameed, *et al*, 2008):

$$Q_e = F C_e^{1/n} \quad (13)$$

Where Q_e is the quantity of solute adsorbed at equilibrium; also called adsorption density, expressed in mg of adsorbate per g of adsorbent; C_e is the concentration of adsorbate at equilibrium, while F and n are empirical constants. By taking logarithms on both sides, the equation gives the more convenient linear form:

$$lnQ_e = lnF + \frac{1}{n} lnC_e \quad (14)$$

The Temkin Isotherm

The isotherm of Temkin developed in 1941 for adsorption in the gas phase was transposed to the liquid phase by Zarrouki in 1990 (Tchuifon, *et al*, 2014). It was generally presented by the following equation:

$$\theta = \frac{RT}{\Delta Q} lnK_0 C_e \quad (15)$$

Where $\theta = \left(\frac{Q_e}{Q_m}\right)$; is the rate of covering of the surface of the adsorbent, K_0 is the equilibrium constant and ΔQ is the change in the energy of adsorption. The linear form of the equation of Temkin is:

$$Q_e = \frac{Q_m RT}{\Delta Q} \ln K_0 + \frac{Q_m RT}{\Delta Q} \ln C_e \quad (16)$$

The value of Q_m, introduced into this equation is obtained from the equation of Langmuir.

Results and Discussions

The properties obtained from the characterization of the adsorbents are presented in Table 1 below. The American Water Work Association has set 0.25 g/cm³ as the lower limit on the bulk density for activated carbon if it has to be of practical use. The bulk densities of the prepared activated carbons given in Table 1 satisfy this condition. The moisture contents of the prepared activated carbons are also reported in Table 1. Their values are greater than those of commercial activated carbons, which are normally lower than 5%. The minimum iodine number recommended by the American Water Work Association for a carbon to be used in removal of low molecular weight compounds is 500 mg/g. The iodine number obtained in this work are within this range. The lower values of pH and pH_{PZC} show that all the three adsorbents have more acid groups on their surfaces.

Table 1: Properties of the activated carbons

Parameter	CAH1	CAH2	CAMH
Bulk density (g/cm³)	0.802	0.826	0.744
Moisture content (%)	8.86	6.93	8.91
pH	5.20	6.30	3.72
pH_{PZC}	3.0	3.45	2.30
Iodine number (mg/g)	476.25	495.30	590.55

Influence of contact time on adsorption

The time of agitation is a very significant parameter in the adsorption process, because it makes it possible to determine the time necessary to reach equilibrium adsorption. Studies on the adsorption of salicylic acid and sulfosalicylic acid of initial concentration 70 mg/L in aqueous solution were carried out with 20 mL solution of each adsorbate, and the results are presented in Figures 1a and 1b. The figures present the evolution of the capacity of adsorption of each compound with time at ambient temperature. The results show that the adsorption process took place in two stages. The first stage occurred very fast, and took place during the first 20 minutes of adsorption. The second stage was much slower and took a longer time. The occurrence of the fast phase can be explained by the fact that, at the start of the process all the sites on the adsorbent are available, and the acid molecules readily occupy them. The slow phase which ended at the inset of equilibrium occurs because the presence of the carboxylic and hydroxyl groups inhibits the adsorption of the organic compounds (Villacanas, *et al*, 2006; Alvarez, *et al*, 2005). In fact, the idea that π-π interactions are put in evidence is highlighted. That is, the attracting groups of electrons in the adsorbate tend to attract the π electrons of the carbon.

The results also reveal that the time to achieve equilibrium adsorption depends on the type of adsorbate compound. Thus, equilibrium for salicylic and sulfosalicylic acids were reached in 100 minutes and 120 minutes respectively. This implies that the kinetics of adsorption is influenced by the molar mass of the adsorbed compound. The larger the molar mass, the longer it takes to get to equilibrium.

Figures 1a and 1b also show that the quantities of salicylic acid adsorbed by the three activated carbons are much greater than those of sulfosalicylic acid under the same conditions. For example, Table 2 below summarizes the maximum quantities of acids adsorbed at equilibrium and the percentage adsorption onto the three activated carbons.

Salicylic acid, which is the compound that is more adsorbed, is also the less soluble. This implies that the capacity of adsorption follows the opposite order of solubility. That is, the more soluble a compound is in water, the lower the quantity of the compound adsorbed. This tendency had also been revealed by other authors (Singh and Yenkie, 2006).

Table 2: Maximum adsorption capacity and percentage adsorption onto the activated carbons

Activated carbon	Maximum adsorption capacity (mg/g)		Percentage adsorption	
	Salicylic acid	Sulfosalicylic acid	Salicylic acid	Sulfosalicylic acid
CAH1	24.10	4.38	82.90	31.67
CAH2	27.85	5.20	92.11	37.57
CAMH	27.96	10.55	92.50	76.22

Influence of mass of the adsorbents on adsorption

To deduce the influence of the mass of adsorbing material on the adsorption of the two compounds, different masses of the activated carbons varying between 25 mg and 200 mg were investigated. Both concentration and volume of adsorbate solution were kept fixed at 70 mg/L and 20 mL respectively. The results are presented in Figures 2a and 2b.

They show that the percentage of elimination of salicylic and sulfosalicylic acids increased with the mass of adsorbent. This can be explained by the fact that by increasing the mass of adsorbent, there is an increase in the number of adsorption sites on the surface of the carbon. It is also observed that the activated carbon prepared from the mixture of precursor materials CAMH, has the greatest percentage of adsorption than the other two carbons under the same conditions.

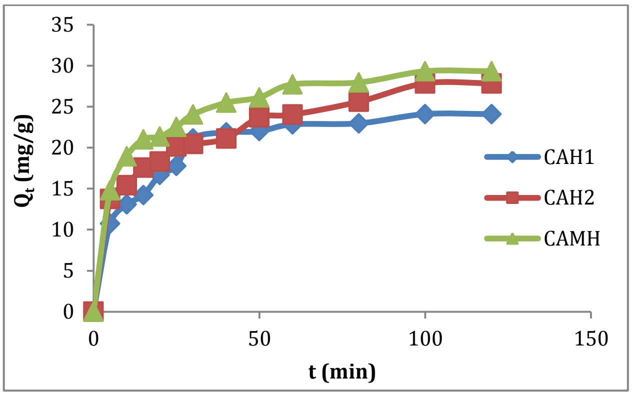


Fig.1a: Effect of contact time on salicylic acid adsorption by the activated carbons. C0 = 70 mg/L, m = 50 mg and V = 20 mL

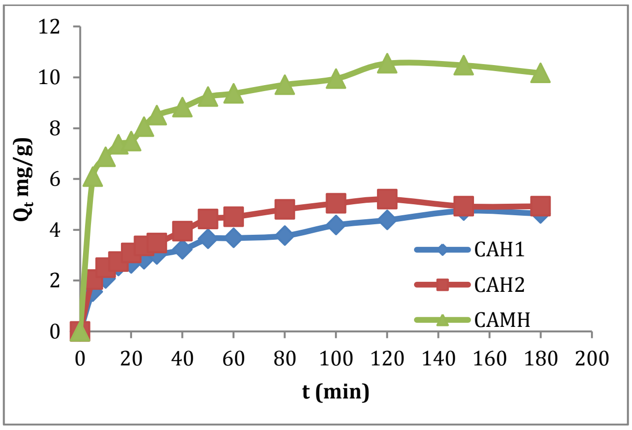


Fig.1b: Effect of contact time on sulfosalicylic acid adsorption by the activated carbons. C0 = 70 mg/L, m = 100 mg and V = 20 mL

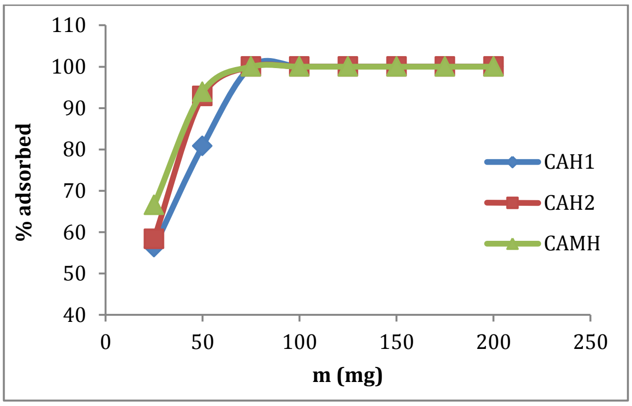


Fig.2a: Influence of the mass of adsorbent on the adsorption of salicylic acid; C_0 = 70 mg/L, and V = 20 mL, t = 100 minutes

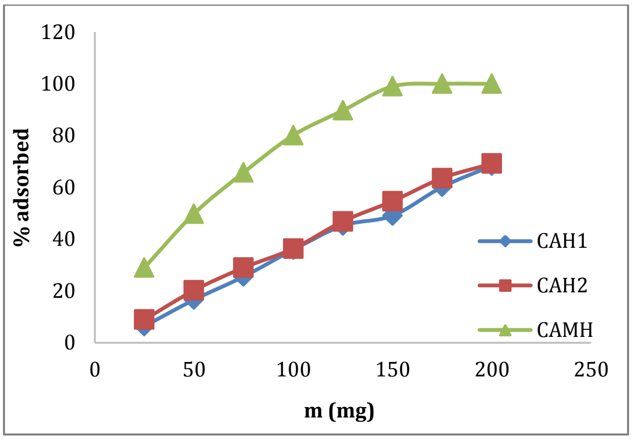


Fig.2b: Influence of the mass of adsorbent on the adsorption of sulfosalicylic acid; C_0 = 70 mg/L, and V = 20 mL, t = 120 minutes

A closer examination of the figures reveals that percentage elimination varies significantly with the type of adsorbent and the adsorbate. With salicylic acid, the capacity of adsorption increases from 56 percent for 25 mg of activated carbon to 100 percent for 100 mg adsorbent. Here, there is no significant difference in adsorption capacity between the activated carbons. With sulfosalicylic acid, the adsorption capacity with 25 mg adsorbent mass was only 6.36 percent for the single material activated carbons CAH1 and CAH2, and 28 percent for the mixed activated carbon, CAMH. 100 percent adsorption was obtained for CAMH at 150 mg adsorbent, while the maximum obtained for the other two was less than 80 percent even at an adsorbent mass of 200 mg.

Influence of pH on adsorption

pH of the solution is one of the most important parameters affecting adsorption processes because it affects the surface charge of the adsorbent as well the degree of ionization of adsorbate (Maleki, *et al*, 2010). To understand the mechanism of adsorption, the pH at the point of zero load (pH_{PZC}) of the adsorbents were determined. The effect of the pH was studied in the interval 2 -7 with an initial concentration of 70 mg/L for each compound. The results obtained are presented on Figures 3a and 3b below. The results show that adsorption of these compounds is favoured for $pH < pH_{PZC}$. The maximum adsorption is observed at a pH of 2 for the two compounds. The pH_{PZC} for the various carbons are 3.00 for CAH1, 3.48 for CAH2 and 2.30 for CAMH. Maximum adsorption at pH = 2, which is lower than the pH_{PZC} for the three carbons can be explained by the fact that, at this pH, the surface of the materials are positively charged. This creates a strong electrostatic interaction between the surface of the material and the adsorbate molecule. The pH also affects the ionization level of adsorbate and thus the load of the molecule. With $pH > pH_{PZC}$, the adsorbate is more soluble, and the negative charges of the surface of the activated carbons increase the electrostatic force of repulsion between adsorbate anions and –OH groups of the surface of the material, and also between the phenolate–phenolate anions in solution resulting in a decrease in the uptake of salicylic and sulfosalicylic acids (Mareno-Castilla, 2004).

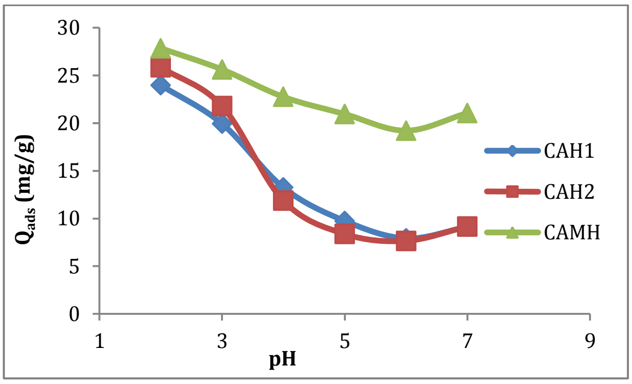


Fig.3a: Influence of pH on the adsorption of salicylic acid

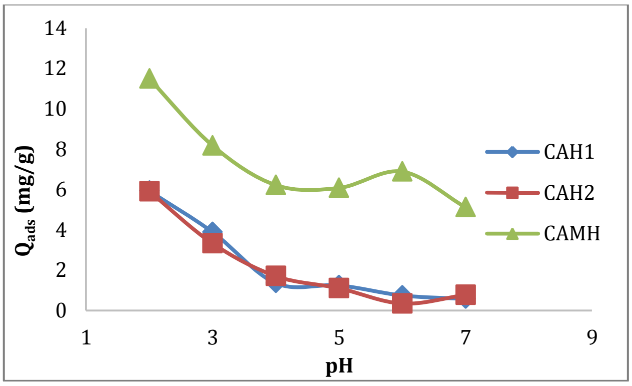


Fig.3b: Influence of pH on the adsorption of sulfosalicylic acid

Influence of initial concentration

The adsorption of a compound on a solid is generally characterized in two ways:

On the one hand, the equilibrium isotherm of adsorption makes it possible to evaluate the affinity of a material as well as its capacity of adsorption;
On other hand, the kinetics of adsorption makes it possible to identify the limiting phenomena in the adsorption process, and it is also a key parameter of the process.

The study of the isotherm of adsorption is fundamental for the determination of the capacity of adsorption and the nature of adsorption. To determine these, the initial concentration of adsorbate was varied, while maintaining constant the other parameters such as pH, volume of the solution, time of contact and the mass of adsorbent. When the initial concentration was increased from 50 to 100 mg/L, the capacity of adsorption for the three carbons was observed to increase. This increase in the capacities of adsorption for the activated carbons with the increase in concentration of salicylic and sulfosalicylic acids can be due to π–π interactions between these organic compounds and the functional groups of the carbon surface. The π-π interactions in most cases are responsible for the mechanism of adsorption of aromatic compound (Bohli, *et al*, 2013; Li, *et al*, 2012). The initial concentration provides a significant driving force to overcome all resistances to mass transfer of all the molecules between the aqueous phases and solids (Juang, *et al*, 1997; Donmez and Aksu, 2002). The profile of the isotherms is controlled by the potential of adsorption which results from electrostatic and dispersive interactions. The energy of adsorption depends on the pore size of the adsorption sites relative to the size of the adsorbate.

Kinetic study of adsorption

Four kinetic models; the pseudo first order, the pseudo second order, the Elovich and the intraparticle diffusion models were used to explain the experimental data obtained in this work. The mechanism by which the process of adsorption takes place, such as chemical reaction, diffusion and mass transfer were examined. The rate constants obtained are shown in Table 3. The correlation coefficients, R^2 were found to be greater than 0.9 for all the three kinetic models. This shows that the mechanism of adsorption can be explained based on any one of the three kinetic models.

Applying the pseudo-first order kinetics, the results obtained are in agreement with a multi-layer adsorption on the surfaces of all the activated carbons. This implies the existence of van der Waal interactions between these organic compounds and the various activated carbons.

These type of interactions thus suggest physical adsorption between the adsorbate and the adsorbent.
Using the pseudo-second order model, the interactions can be said to be chemical in nature; thus the bonds between adsorbate and adsorbent are covalent (Ho, 2006). The linear form of the model is given in Figure 5. From the result, one can say that chemical adsorption dominates the process of adsorption of salicylic acid and sulfosalicylic acid onto the various activated carbons. The initial rates of adsorption (h) of salicylic and sulfosalicylic acids are observed to be relatively high compared to the adsorption of other organic compounds. The high initial rates imply that their adsorption is fast right from the first minutes, as can be observed from the influence of the time of contact. These results are similar to those obtained from a previous study (Tsai and Lai, 2006).

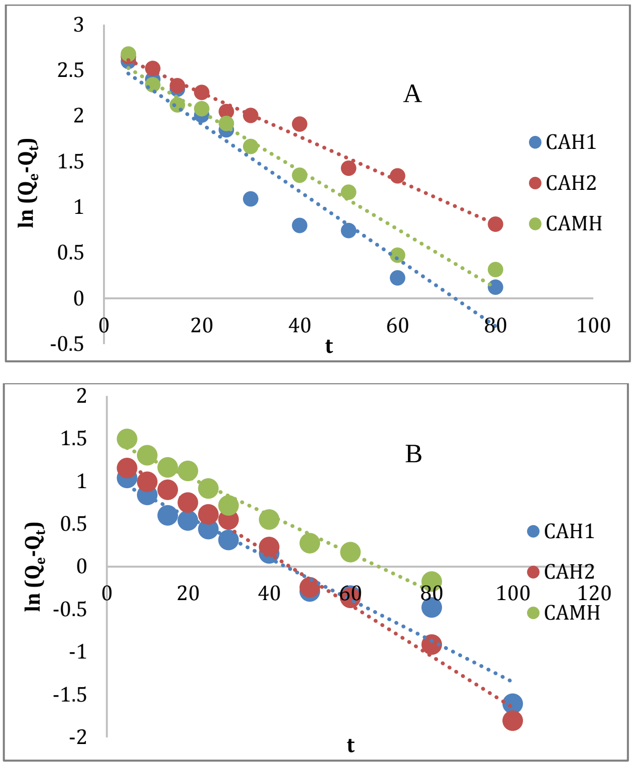


Fig.4: Pseudo-first order kinetic plots for the removal of (A) salicylic acid, and (B) sulfosalicylic acid

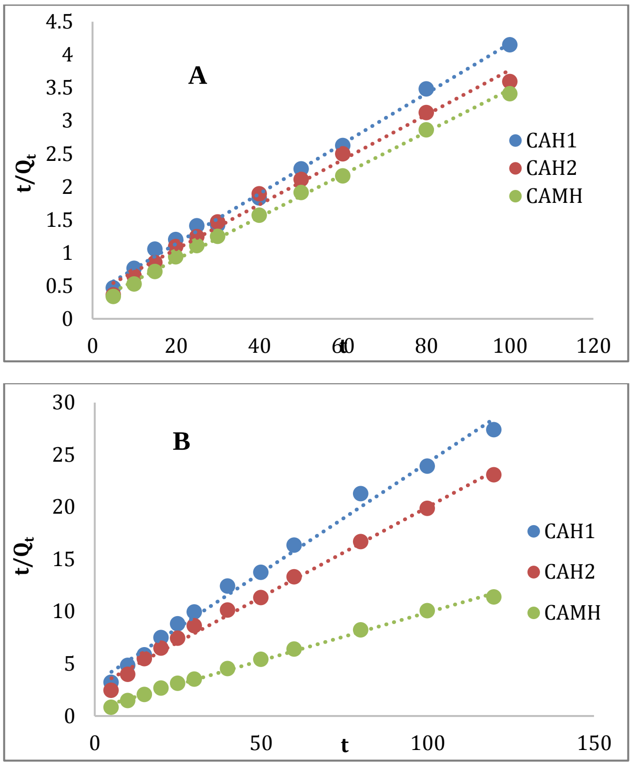


Fig.5: Pseudo-second order kinetic plots for the removal of (A) salicylic acid, and (B) sulfosalicylic acid

As seen from Table 3, it is evident that the adsorption of salicylic and sulfosalicylic acids onto the activated carbons adequately follows the pseudo second order kinetic model, as the correlation coefficients are higher than 0.99 for both adsorbates. The applicability of the pseudo-second order kinetic model shows that the rate limiting step is chemisorption. This involves interactions caused by sharing or exchange of electrons between sorbent and sorbate. (Ho and Mc Kay, 1998).

Applying the Elovich model (Figure 6), the presence of various functional groups such as carbonyls, carboxylics and lactones derived from the structure of the activated carbon suggest that their surfaces contain several types of pores, and they offer with various types of interactions (Wu, *et al*, 2005).

Any kinetic expression or mass transfer is likely to be total. The equation of Elovich is also used successfully to describe the kinetics of the second order by supposing that real solid surfaces are energetically heterogeneous (Rudzinski and Panczyk, 2002). It depends on the magnitudes of the Elovich coefficients α and β, and they represent respectively the initial speed of sorption and the constant of desorption. Based on the equation of Elovich, the constants β, α and t_0 are related by the equation

$$t_0 = {}^{1}/_{\alpha\beta} \qquad (21)$$

The constant t_0 and β can be commented upon as follows:

- Initially, the assumption that $t >> t_0$ is justified because values of t_0 are low.
- Secondly, the value of 1/β obtained is large for the salicylic acid. Such a tendency suggests a multiplicity of the number of sites available for adsorption (Wu, *et al*, 2005).
- The affinity of the various adsorbates for the adsorbents is once more confirmed with the kinetic model of Elovich as is exhibited by the high values of the correlation coefficients.

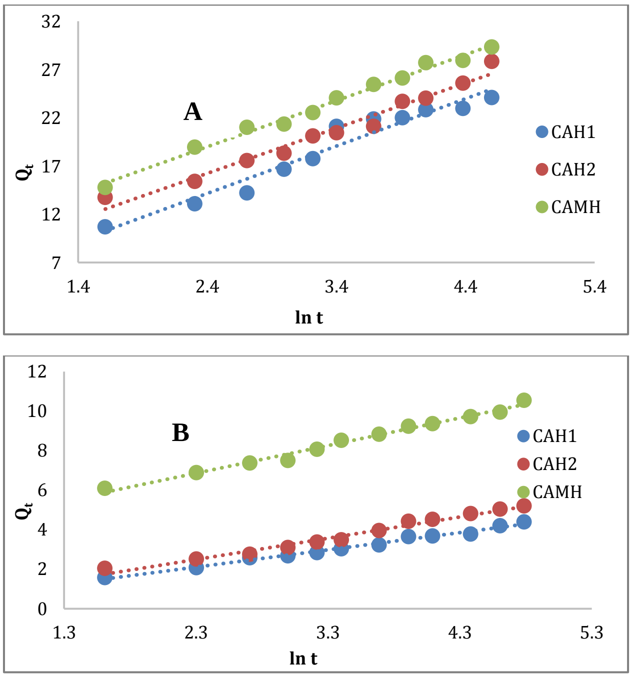


Fig.6: Elovich kinetic plots for the removal of (A) salicylic acid, and (B) sulfosalicylic acid

These results bring into play the existence of sites adsorption of various energies at the surface of the materials. That is, they highlight the heterogeneity of the surface of the activated carbons. This fact strongly suggests that the adsorption is limited to chemical interactions between the adsorbates and the adsorbents which lead to a dominance of the prevalence of chemical adsorption in the adsorption process (Chueng, *et al*, 2001; Juang, Chen, 1997).

Intraparticle diffusion study

The mechanism of adsorption is generally considered to involve three steps, one or any combination of which can be the rate-controlling mechanism: These steps are:

(i) Mass transfer across the external liquid film surrounding the particle;
(ii) Adsorption at a site on the internal or external surface of the adsorbent; and the energy will depend on the binding process: whether physical or chemical. This step is often assumed to be extremely rapid;
(iii) Diffusion of the adsorbate molecules to an adsorption site either by a pore diffusion process through the liquid film process or by a solid surface diffusion mechanism.
From the plots of Q_t versus $t^{0.5}$ multi-linearity was observed for the various phenolic compounds, (Figure 7), indicating that the adsorption process takes place in two steps. As seen from the figure, the plot was not linear over the whole time range, implying that more than one mechanism affected the adsorption process. The first portion describes the gradual adsorption stage or external mass transfer effects. These lines do not pass through the origin, indicating that the intraparticle diffusion is not the only process that can control the kinetics of adsorption. The second portion is attributed to the final equilibrium stage for which the intraparticle diffusion started to slow down due to the extremely low amount of phenolic compounds left in the solution.

Adsorption isotherm

To determine the capacity of adsorption of the compounds on various carbons, the experimental data was verified by using the isotherms of Langmuir, Freundlich and Temkin. The parameters for these adsorption models were calculated using the linear form of the equations of the isotherms.

Isotherm of Langmuir

Figure 8 represents the linear form of the Langmuir isotherm. This isotherm quantitatively describes the formation of only a monolayer of adsorbate on the external surface of the adsorbent, after which, no further adsorption takes place. This result also indicates the monolayer adsorption of the acids onto a surface containing a finite number of identical sites, and that, no migration of adsorbate takes place in the plane of the surface after adsorption. It thereby represents the equilibrium distribution of adsorbate between solid and liquid phases (Dada, *et al*, 2012). The high values of the correlation coefficient (R^2) obtained for this model show that the model correctly describes the adsorption data of salicylic and sulfosalicylic acids onto the activated carbons. The essential characteristic of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter R_L, defined by Equation 12. Its values as presented in Table 3, ranging between zero and one, indicate a favorable adsorption.

Isotherm of Freundlich

This isotherm is generally used to describe adsorption onto heterogeneous surfaces. The correlation coefficients were found to be greater than 0.9 (Figure 9). The maximum adsorption capacity Q_m can be evaluated using the Freundlich constant K_f given by the following expression (Haley, 1952), (Hamdaoui and Naffrechoux 2005):

$$K_f = Q_m / C_0^{\frac{1}{n}} \qquad (22)$$

By considering C_0, the highest value of the initial concentration, the values of Q_m according to Freundlich can be calculated. By comparing these values with the values of Q_m found using the Langmuir isotherm, it appears that $\Delta Q_m < 3$ mg/g for some cases and approximately equal to zero for others.

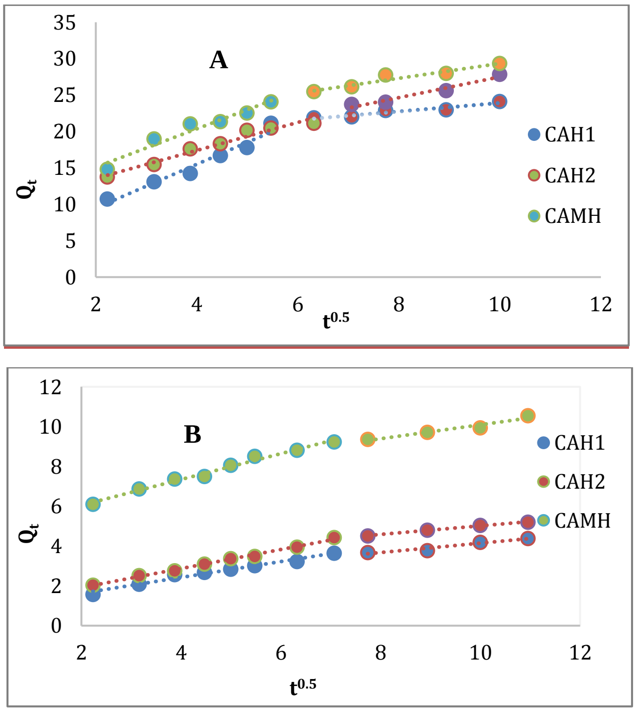


Fig.7: Plots of intraparticule diffusion models of adsorption of (A) salicylic acid and (B) sulfosalicylic acid

The values of Q_m are close to those obtained from Langmuir isotherm. The means that the assumption of the existence of different types of sites of adsorption of different energy, but having the same entropy, distributed according to an exponential law based on the heat of adsorption is in agreement with experiment (Hamdaoui and Naffrechoux, 2005; 2007).

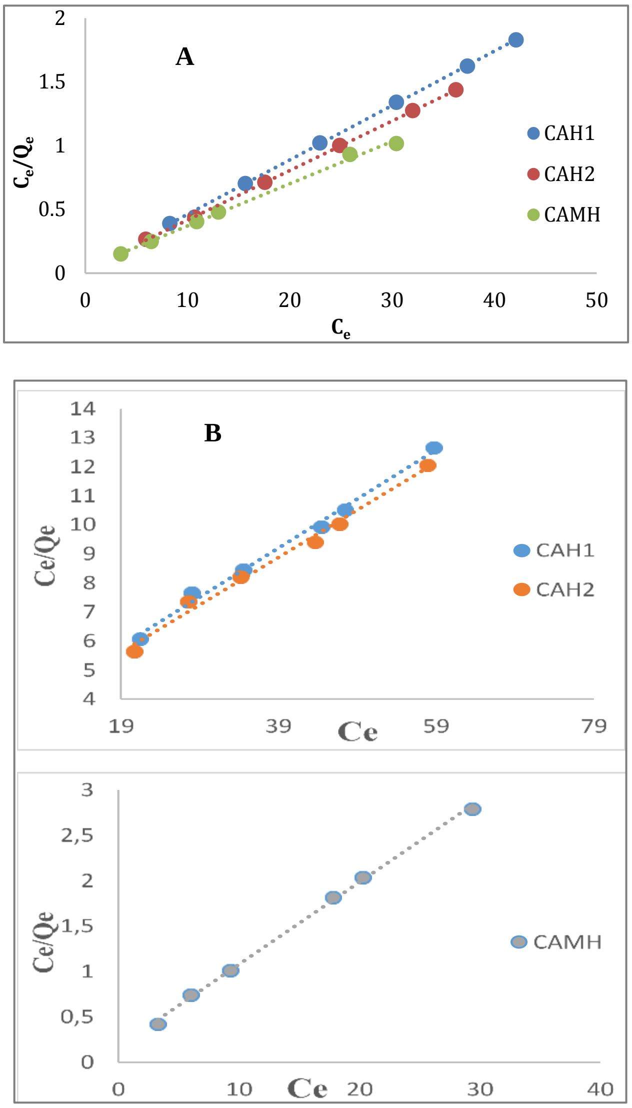
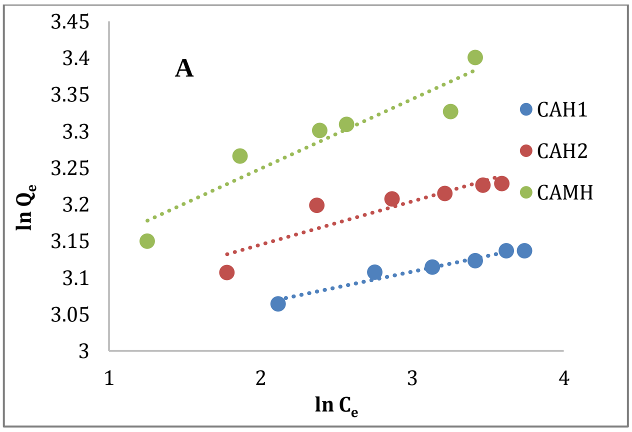


Fig.8: Linear plot of the model of Langmuir (A) salicylic acid and (B) sulfosalicylic acid



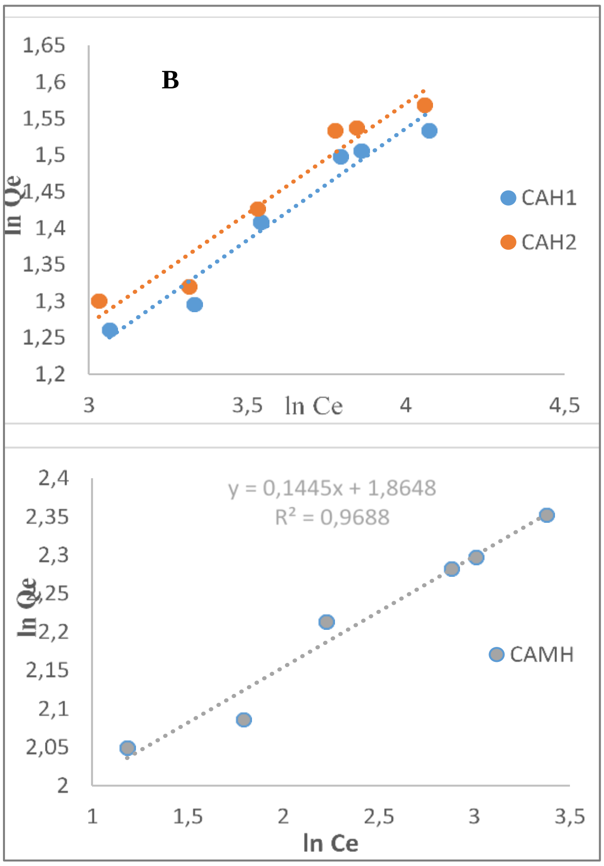


Fig.9: Linear plots of the Freundlich model for (A) salicylic acid and (B) sulfosalicylic acid

These results favour of the applicability of the equation of Freundlich in the study of the adsorption isotherms of these compounds onto the activated carbons.

Isotherm of Temkin

The Temkin isotherm is presented in Figure 10. This isotherm contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. The isotherm assumes that: (i) the heat of adsorption of all molecule in the layer decreases linearly with coverage due to adsorbate-adsorbate interactions, and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy (Kavitha and Namasivayam, 2007). In accordance with the energies, the variation of the energy of adsorption ΔQ resulting from the linearization of the Temkin model is always positive for the two molecules and the three adsorbents. A positive value of energy means that the process of adsorption is exothermic.

Table 3: Kinetic parameters of adsorption of salicylic and sulfosalicylic acids onto activated carbon

Kinetic models	Adsorbate	parameters	CAH1	CAH2	CAMH
Pseudo-first order	**Salicylic acid**	K_1 (1/min)	0.037	0.024	0.032
		Qe (mg/g)	14.117	15.333	14.655
		R^2	0.9132	0.9854	0.969
	Sulfosalicylic acid	K_1 (1/min)	0.024	0.030	0.023
		Qe (mg/g)	2.896	3.883	4.4929
		R^2	0.9527	0.9905	0.978
Pseudo-second order model	**Salicylic acid**	K_2 (g/min.mg)	0.004	0.003	0.0041
		Qe (mg/g)	26.385	29.412	31.056
		h (mg/min.g)	2.640	2.675	3.976
		R^2	0.9961	0.9894	0.9976
	Sulfosalicylic acid	K_2 (g/min.mg)	0.014	0.0108	0,012
		Qe (mg/g)	4.742	5.570	10.834
		h (mg/min.g)	0.315	0.360	1.425
		R^2	0.9918	0.9939	0.9967
Elovich model	**Salicylic acid**	β (g/mg)	0.204	0.214	0.220
		α (mg/g.min)	7.957	13.699	25.154
		t_0 (min)	0.617	0.341	0.181
		R^2	0.9475	0.9707	0.9899
	Sulfosalicylic acid	β (g/mg)	1.147	0.929	0.717
		α (mg/g.min)	0.979	1.094	19.095
		t_0 (min)	0.890	0.984	0.073
		R^2	0.9870	0.9793	0.9885
Intraparticle diffusion model	**Salicylic acid**	K_{id1} (mg/g.min$^{-0.5}$)	3.0096	1.9272	2.6276
		C_1 (mg)	3.4508	9.7019	9.8448
		R^2	0.9549	0.9638	0.9478
		K_{id2} (mg/g.min$^{-0.5}$)	0.5839	1.4278	1.0096
		C_2 (mg)	18.079	13.244	19.232
		R^2	0.9189	0.955	0.9334
	Sulfosalicylic acid	K_{id1} (mg/g.min$^{-0.5}$)	0.3990	0.4796	0.6486
		C_1 (mg)	0.8218	0.9425	4.7543
		R^2	0.9722	0.9943	0.9857
		K_{id2} (mg/g.min$^{-0.5}$)	0.2366	0.2172	0.3507
		C_2 (mg)	1.7735	2.8414	6.5904
		R^2	0.9351	0.9947	0.9464

Table 4: Equilibrium parameters of adsorption of salicylic and sulfosalicylic acids

Isotherms	Adsorbates	parameters	CAH1	CAH2	CAMH
Langmuir model	**Salicylic acid**	K_L (L/mg)	1.177	1.320	0.838
		Q_m (mg/g)	23.474	25.773	30.211
		R^2	0.9999	0.9999	0.9965
		R_L	0.00859	0.00766	0.0007
	Sulfosalicylic acid	K_L (L/mg)	0.065	0.065	0.521
		Q_m (mg/.g)	5.921	6.124	11.038
		R^2	0.9929	0.9893	0.9984
		R_L	0.1589	0.1578	0.0228
Freundlich model	**Salicylic acid**	K_f	19.482	20.633	21.306
		Qe (mg/g)	23.7504	27.0557	32.9224
		1/n	0.0432	0.0591	0.0949
		R^2	0.9585	0.8168	0.8853
	Sulfosalicylic acid	K_f	1.3668	1.4401	6.4546
		Qe (mg/g)	5.2601	5.4358	12.1996
		1/n	0.3059	0.3015	0.1445
		R^2	0.9560	0.9417	0.9688
Temkin model	**Salicylic acid**	ΔQ (KJ/mol)	60.519	45.377	29.835
		K (L/mg)	$5.17x10^8$	$2.01x10^6$	$4.01x10^3$
		R^2	0.9613	0.8259	0.8896
	Sulfosalicylic acid	ΔQ (KJ/mol)	11.815	11.981	20.995
		K (L/mg)	0.764	0.807	104.978
		R^2	0.9588	0.9422	0.9702

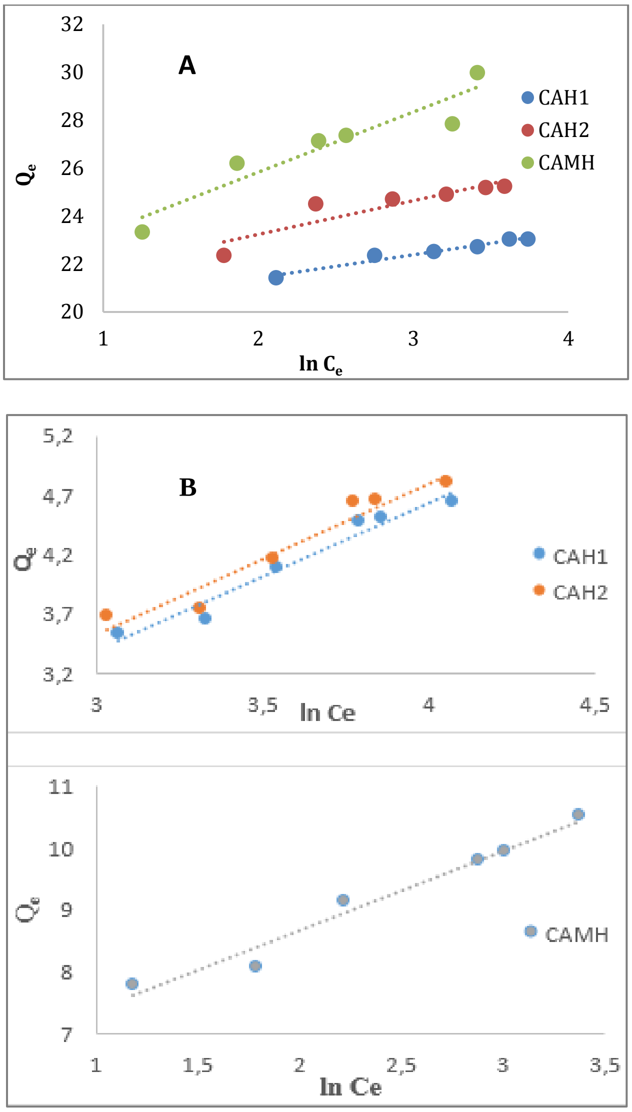


Fig.10 Linear plot of the model of Temkin (A) salicylic acid and (B) sulfosalicylic acid

Conclusion

The study of the adsorption of two phenolic compounds namely salicylic and sulfosalicylic acids with three activated carbons prepared from local biomass was realized in order to understand the mechanism of adsorption of these compounds from aqueous solution. The activated carbons used, present in general, a strong acid character and a good affinity for the compounds studied. The kinetic study made it possible to show the heterogeneity of the surface of the various activated carbons, and also that the kinetic model of pseudo second order better describes the adsorption of these compounds. From the study of isotherms, it appears that the surface of the activated carbons present sites of adsorption of different energies. It is also shown by these studies that it is almost impossible to highlight the real type of adsorption between chemisorption and physisorption, because these modes participated during the adsorption process of these phenolic compounds. The adsorption of the individual phenolic compounds is mainly influenced by the low solubility of the molecules in solvent.

Acknowledgment

The authors acknowledge the financial support from the International Foundation for Science (IFS) and Third World Academy of Science (TWAS). The authors thank Pr Sopbue F. Emmanuel and Mr. Tchieno M. Francis Merlin in Department of Chemistry, University of Dschang (Cameroon) for their interest discussion about this work and also Mrs. Nkwaju Y. Rachel and Mr. Lekene N. Rene Blaise in the Department of Chemistry, University of Yaoundé 1, Physical and Theoretical Chemistry Laboratory (Cameroon), for all their help.

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