Research Article

IJCRR
Section: General Science
Sci. Journal
Impact Factor 4.016

KINETICS AND EQUILIBRIUM STUDIES OF THE ADSORPTION OF PHENOL AND METHYLENE BLUE ONTO COLA NUT SHELL BASED ACTIVATED CARBON

Lekene Ngouateu R. B., Kouoh Sone P M. A., Ndi Nsami J., Kouotou D., Belibi Belibi P. D., Ketcha Mbadcam J.

Physical and Theoretical Chemistry Laboratory, Department of Inorganic Chemistry, Faculty of Science, University of Yaoundé I, Yaoundé – Cameroon

ABSTRACT

The aim of this work was to study the removal of methylene blue (MB) and phenol from aqueous solution using powder activated carbon prepared from cola nut shells chemically activated with KOH solution. The effect of contact time, adsorbent dose, pH and initial concentration has been studied using batch adsorption method. Given the base line for the results, the percentage removal of MB and phenol were 98.19 % and 61.81 % respectively. The maximum adsorption of MB and phenol occur at pH 8 and 6. Also the quantity adsorbed decreases with the adsorbent dose for both adsorbates. The quantity adsorbed of MB increases with increased in initial concentration whereas reverse result was observed with phenol. The adsorption equilibrium data were confronted to Langmuir, Freundlich, Tempkin and Dubinin-Kaganer-Radushkevich isotherms models. The Langmuir model describes better the adsorption with maximum monolayer adsorption capacities of 65.79 mg.g-1 and 6.22 mg.g-1 for MB and phenol respectively. The kinetics of methylene blue and phenol adsorption were also discussed using pseudo-first-order, pseudo-second-order, Elovich, mass transfer and intra-particle diffusion models. The adsorption process follows the pseudo-second-order and mass transfer kinetic models respectively for methylene blue and phenol owing to their high correlation coefficient. This study shows that the prepared activated carbon can be used as low cost alternative adsorbent for removal of both phenol and MB.

Key Words: Adsorption, Activated carbon, Equilibrium, Kinetics, Methylene blue and Phenol

INTRODUCTION

Many industries discharge wastewaters containing many hazardous substances such as phenols, heavy metals and dyes. The contamination of water by industrial activities is the source of problems to human health and environment (Hameed et al, 2007a).

MB in industries has wide variety of application such as colouring of papers, dyeing textiles and cosmetics. Consequently, their effluents contain notable amounts of this dye stuff (Shen et al, 2009; Reddy et al, 2012). On the other hand, phenol found mostly in pesticides, pharmaceuticals, petro-chemicals, steel manufacturing, etc. (Alam et al, 2006; Varghese et al, 2004; Isichei and Okieimen, 2012) causes several problems. In addition, phenol and the MB are very harmful to humans and other aquatic organisms (Hameed et al, 2007b; Ekpete et al, 2012). The presence of MB in water inhibits sun light diffusion into the water, which reduces the photosynthetic process of aquatic plants (Idris et al, 2012a; Ndi et al, 2013). The ingestion of methylene blue and phenol causes many problems like vomiting, mental confusion, diarrhea, dark urine, cyanosis, tissue necrosis and increased heart bit rate (Hameed et al, 2007a; Karabacakoğlu et al, 2008).

Thus, it is important to treat wastewaters before their rejection into the nature. And for this purpose, many methods of removing these pollutants have been used such as chemical precipitation, filtration, ion exchange, reverse osmosis, ultra-filtration, biological degradation, membrane separation, solvent extraction and adsorption. These methods differ in their efficiency to remove

Corresponding Author:
Ketcha Mbadcam J., Physical and Theoretical Chemistry Laboratory, Department of Inorganic Chemistry, Faculty of Science, University of Yaoundé I, Yaoundé – Cameroon; E-mail: jketcha@yahoo.com

Received: 13.02.2015 **Revised:** 10.03.2015 **Accepted:** 09.04.2015

dyes and phenol and are very expensive (Moraitopoules et al, 2009). However, adsorption remains the outmost process because of its simplicity, high efficiency and easy recovery (Ndi Nsami et al, 2013).

In the scientific literature, many adsorbents have been used such as zeolite, clay, silica gel, resins, activated alumina and activated carbon (Ketcha et al., 2007; Ketcha Mbadcam et al, 2012a). Activated carbon is the most widely used adsorbents owing to its well-developed pore structure, large active surface area, good mechanical properties and multiple functional groups at their surface (Wu et al, 2005, Kouotou et al, 2013). There are many precursors from which it can be prepared and some of these precursors include corn cobs (Tsai et al, 2001; Ketcha Mbadcam et al, 2012a), apricot stone (Kobya et al, 2005), sugar bagasse, coconut shells (Jaguaribe et al, 2005), peanut hull (Guler et al, 2007), rattan sawdust (Hameed et al, 2007a), bamboo (Hameed et al 2007b), hazelnut bagasse (Karabacakoğlu et al, 2008), cotton stalk fibre (Kunquan et al, 2009), rice husk (Yahaya et al, 2011), oil palm shell (Kouotou et al., 2012), cola nut shell (Ndi et al, 2013); olive stone (Hanen and Abdelmottaleb, 2013)

The aim of the present study was to examine the adsorption capacities of MB and phenol from aqueous solution onto activated carbon prepared from cola nut shells activated with KOH using batch system. The effects of factors such as contact time, adsorbent dose, pH and initial concentration were investigated. The kinetics and equilibrium data were confronted to several models.

MATERIALS AND METHODS

Preparation of adsorbent

The cola nut shells were initially washed with tap water followed by distilled water, sun dried and mechanically ground using a grinding machine (Retch) then sieved through a sieve (Retch) to get geometrical size less than 1.5 mm. The prior sieved cola nut shells was kept in an oven at 110 °C for a period of 24 hours, then allowed to cooled to room temperature, in a desiccator containing $CaCl_2$ (drying agent) for 30 min. It was removed from the desiccator and a mass reagent ratio 1:1 was applied, mixed, and dried for 24 hours at 110 °C in an oven (Ndi et al, 2013).

The carbonization and activation were accomplished in a one-single step by carrying out thermal transformation of cola nut shells impregnated with KOH as activating agent in the absence of air in a Carbolite furnace (OSI) at 500 °C for 1 hour as resident time. After activation, the furnace was allowed to cool to room temperature. The pyrolysed carbons were leached with 1 % HCl (v/v) for 2-3 hours and washed several times with distilled water until a neutral pH was achieved. The activated carbon obtained was later dried in an oven at 110 °C for at least 24 hours and kept for further application (Ndi Nsami et al, 2013).

Characterization of adsorbent

The surface functional groups of the prepared activated carbon were estimated using Fourier Transform Infrared (FTIR) spectroscopy (Alpha - Bruker). The FTIR spectra of our sample were recorded within 400-4000 cm-1. The BET specific surface area, the total pore volume and the pore size of activated carbon were determined by standard multipoint techniques of nitrogen adsorption using Micromeritrics ASAP 2020 equipment. The iodine number which is a measure of micropore content of the activated carbon is determined by the American Standard for Testing of Materials (ASTM D2866-94).

Preparation of solutions

All the reagents used in this study were of analytical grade. Two stocks solutions of MB and phenol of concentration 50 $mg.L^{-1}$ and 1000 $mg.L^{-1}$ respectively were prepared by dissolving 0.050 g of MB and 1.000 g of phenol separately in 1000 mL volumetric flask. These solutions were stirred until total dispersion and the volume completed with distilled water up to mark. These solutions were stirred on a magnetic agitator for 6 hours to homogeneity. All the experimental solutions were prepared by diluting the stock solution to the required concentration.

Batch adsorption study

The batch adsorption was carried out at room temperature. The effects of contact time, adsorbent dose, pH of solution and the initial concentration of these adsorbates were studied. In each experiment, 20 mL of MB or phenol solution of known concentration were mixed with a known mass of activated carbon. The pH of the mixture was adjusted either with 0.1 N HCl or 0.1 N NaOH solutions. The suspension was stirred for a given interval of time, using a magnetic agitator and stirrer at a controllable speed. After agitation, the suspensions were filtered using Whatman No°1 filter paper. The concentration of phenol after adsorption was determined using a back titration method as described by Jeffery et al and that of MB was determined using a UV-visible spectrophotometer (CORNING, 256) at the maximum absorption wavelength of 668 nm.

The quantity adsorbed by a unit mass of an adsorbent at equilibrium (Q_e) and the adsorption percentage were calculated using the following relations:

$$Q_e = \frac{(C_0 - C_e)}{m} \times V \quad (1)$$

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Where C_e is the concentration of adsorbate at equilibrium (mg.L-1); C_0 is the initial concentration of adsorbate (mg.L-1); V is the volume of adsorbate (mL); and m is the mass of adsorbent (mg).

RESULTS AND DISCUSSION

Results

Characterisation of prepared activated carbon

The FTIR spectrum of activated carbon is shown in (Fig. 1) with the following significant absorption bands: 3321 cm^{-1}; 873, 802, 752 cm^{-1}; 1574 cm^{-1}; 1163 cm^{-1}; 1089.9 cm^{-1}

The physicals properties of activated carbon are shown in table 1.

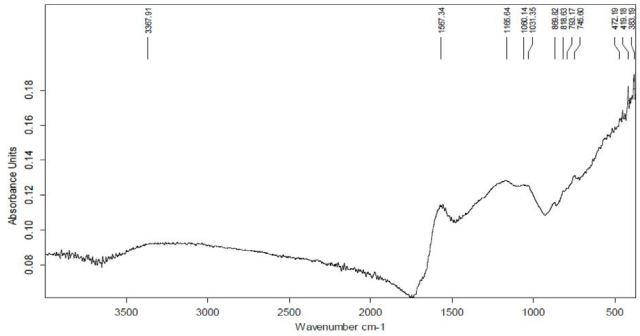

Figure 1: FTIR spectrum of AC

Contact time

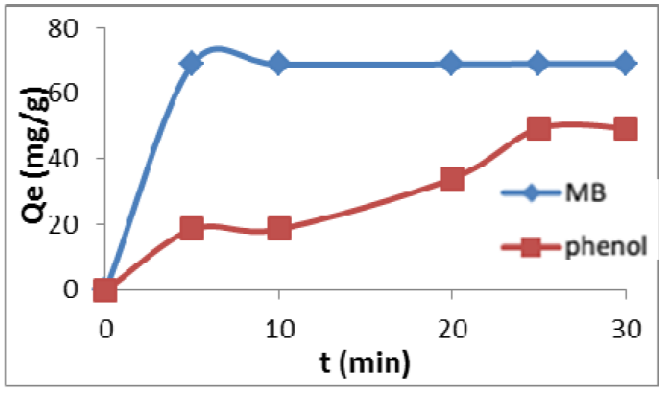

Figure 2: Effect of contact time

The effect of contact time of both adsorbates was determined by agitating 20 mL solution of phenol of initial concentration of 200 $mg.L^{-1}$ with 0.05 g of activated carbon and 20 mL of MB solution with initial concentration of 18 $mg.L^{-1}$ and 0.005 g of AC. The experimental results obtained are shown in Fig. 2. The adsorption rate of phenol was slow within the first 10 minutes, and then increased rapidly and reaches equilibrium at 25 minutes.

Adsorbent dose

To study the effect of adsorbent dose on the adsorption of phenol and MB, a series of adsorption experiments were carried out with different adsorbent mass varying from 0.005 to 0.025 g at initial concentration of 18 $mg.L^{-1}$ for MB and from 0.05 to 0.2 g at initial concentration of 200 $mg.L^{-1}$ for phenol. Results (Fig. 3) showed that with an increase in activated carbon dose, the adsorption capacity decreases.

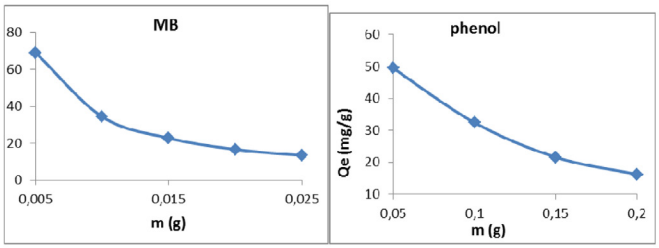

Figure 3: Effect of adsorbent dose

Effect of pH

The pH is an important parameter that influences adsorption of pollutants from aqueous solutions, because it affects both the surface of adsorbent and adsorbate (Jadhav and Vaujara, 2004; Tagne et al, 2013). In this work, the pH was varied between 2 and 10 using 200 $mg.L^{-1}$ of initial phenol concentration and 0.05 g of activated carbon, 18 $mg.L^{-1}$ initial MB concentration and 0.005 g of activated carbon

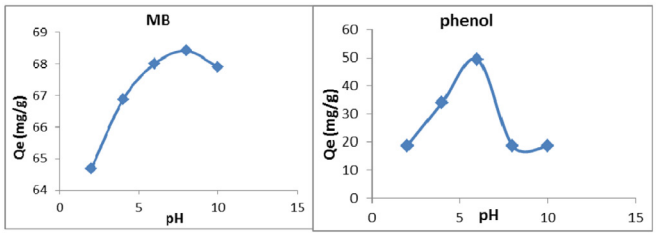

Figure 4: Effect of pH

Effect of initial concentration

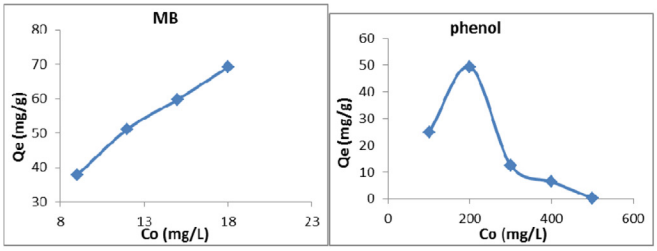

Figure 5: Effect of initial concentration

The effect of initial concentration of adsorbents on adsorption of phenol and MB was carried out on different concentrations ranging from 100, to 500 mg.L^{-1} for phenol and 9 to 18 mg.L^{-1} for MB.

Adsorption isotherm models

An adsorption isotherm is the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium at constant temperature. In order to successfully represent the dynamic adsorptive behaviour of any substance from the fluid to the solid phase, it is important to have a satisfactory description of the equilibrium state between the two phases composing the adsorption system (Ndi Nsami et al, 2013). Classical adsorption models are used to describe the equilibrium established between adsorbed component on the adsorbent and unadsorbed component in solution (represented by adsorption isotherms). Langmuir, Freundlich, Dubini-Radushkevich (D-R) and Tempkin adsorption models were used to analyse the equilibrium data of adsorption of both phenol and methylene blue onto the activated carbon.

Langmuir adsorption isotherm: The Langmuir adsorption equation is one of the most common isotherm equations for modelling equilibrium data in solid-liquid systems. This equation is based on three assumptions: (i) - Adsorption cannot proceed beyond monolayer coverage. (ii) - All the surface sites are equivalent and can accommodate at most one adsorbed atom. (iii) - The ability of a molecule to be adsorbed at a given site is independent of the occupation of neighbouring sites (Ketcha Mbadcam et al, 2011). The general form of the Langmuir equation is:

$$Q_e = Q_m \frac{bC_e}{1+bC_e} \quad (3)$$

where, C_e is the equilibrium concentration (mg.L^{-1}), Q_e is the amount of adsorbate adsorbed per unit mass of the adsorbent at equilibrium (mg/g), b is the Langmuir adsorption constant (L.mg^{-1}) and Q_m is the maximum amount of per unit mass of adsorbent to form a complete monolayer on the surface (mg/g). The linear form of this equation is given below:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \quad (4)$$

The effect of isotherm shape can be used to predict whether an adsorption system is "favourable" or "unfavourable". The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter,R_L, which is defined by the following relationship:

$$R_L = \frac{1}{1+bC_0} \quad (5)$$

The value of R_L indicates the type of the isotherm to be either unfavourable ($R_L > 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Ketcha et al, 2012b).

Freundlich adsorption isotherm: The Freundlich equation is an equation based on adsorption on a heterogeneous surface. Its general form equation is given by equation (6) (Anagho Gabche et al, 2013):

$$Q_e = K_F C_e^{1/n} \quad (6)$$

where, Q_e is the quantity of solute adsorbed at equilibrium, also called the adsorption density (mg.g^{-1}), C_e is the concentration of adsorbate at equilibrium (mg.L^{-1}), K_F and n are empirical constants dependent on several factors. The linear form is given by taking the logarithm on both as:

$$lnQ_e = lnF + \frac{1}{n} lnC_e \quad (7)$$

Dubinin-Radushkevich (D-R): This model envisages the heterogeneity of the surface energies and can be written in the following linear form (8) (Ketcha Mbadcam et al, 2012b).

$$lnQ_e = lnQ_m - \beta\varepsilon^2 \quad (8)$$

where, $\varepsilon = RTln(1+\frac{1}{C_e})$ known as Polanyi Potential.

The mean sorption energy, E (kJ/mol), which is defined as the free energy transfer of one mole of solute from infinity of the surface of the adsorbent, can be calculated using the calculated value of β, from:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (9)$$

if the magnitude of E is between 8 and 16 kJ.mol^{-1}, the sorption process is supposed to proceed via chemisorption, while for values of $E < 8$ kJ.mol^{-1}, the sorption process is of physical nature (Ranjan et al, 2009).

Tempkin adsorption isotherm: Tempkin isotherm assumes that the heat of adsorption decreases linearly with the coverage due to adsorbent - adsorbate interaction (Tagne et al, 2013). The Tempkin isotherm has generally been applied in the following linear form:

Table 1: Physicals properties of activated carbon

	Surface area (m².g^{-1})	Pore volume (cm³.g^{-1})	Pore size (nm)	Iodine number (mg.g^{-1})
Activated carbon	2.0448	0.0048	9.4203	513.9450

Table 2: Isotherms models parameters

Adsorbant		MB	Phenol
Langmuir	R2	0,9875	0,8956
	Qm	65,7895	6,2228
	KL	152	0,0167
Freundlich	R2	0,8263	0,6595
	KF	74,79	450,1136
	1/n	0,118	0,6633
D-R	R2	0,8732	0,2104
	K	3.10-9	0,0002
	Qm	68,1492	13,6127
	E	12,9.103	50
Tempkin	R2	0,843	0,4619
	KT	130,67.103	918,47055
	bT	404,1057	206,7055

Table 3: Kinetic models parameters

		MB	Phenol
Pseudo first order	R2	0.7514	0.8929
	K1	0.0355	0.0497
	Qe	0.3130	43.8029
Pseudo second order	R2	1	0.5552
	K2	3.4×10-5	10.8176
	Qe	1428.5714	3.0713
	h	63.3876	102.0412
Elovich	R2	0.7464	0.8354
	α	2.58×10204	7.6784
	β	6.8871	0.0525
Mass transfer	R2	0.9302	0.9418
	K0	0.0002	0.0450
	lnD	2.8446	3.5291
Intrapartcle diffusion	R2	0.8243	0.8969
	Kid	0.0843	10.8990
	C	68.672	-10.330

generally been applied in the following linear form:

$$Q_e = \frac{RT}{B_T}(lnA_T + lnC_e) \quad (10)$$

where, A_T (L.g^{-1}) is the Tempkin constant, B_T (J.mol^{-1}) is a constant related to heat of sorption, R is the perfect gas constant (8.314 J.mol^{-1}) and T the absolute temperature (K).

The data obtained from these studies have been tested with the Langmuir, Freundlich, Dubinin-Radushkevich and Tempkin linearized equations. The results are summarized in Table 2.

Kinetics adsorption models

In the present work, the kinetics of adsorption of both phenol and MB onto activated carbon was studied using five kinetic models:

***Pseudo – first-order kinetic model*:** the pseudo-first-order equation of Lagergren is generally expressed as follows (Largengren, 1898 Hameed et al, 2007a):

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \quad (11)$$

where, Q_e and Q_t refer to the amount of pollutant adsorbed (mg.g^{-1}) at equilibrium and at any time, t (min), respectively, and k_1 is the equilibrium constant of pseudo-first-order sorption (min^{-1}). Integration of equation (11) for the boundary conditions; t = 0 to t and Q_t = 0 and it rearrangement gives:

$$\log(Q_e - Q_t) = logQ_e - \frac{k_1}{2.303}t \quad (12)$$

Pseudo-second-order kinetic model: If the rate of sorption is a second order mechanism, the pseudo-second-order chemisorption kinetic rate is expressed as (Ho et al, 2000; Essomba et al, 2014):

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (13)$$

where, k_2 is the rate constant of pseudo-second-order sorption (g.mg^{-1}.min^{-1}). The integrated and rearranged form of equation (13) is:

$$\frac{1}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} \quad (14)$$

The initial adsorption rate h (mg.g^{-1}.min^{-1}), when t tends to 0 is given by:

$$h = k_2 Q_e^2 \quad (15)$$

***Elovich kinetic model*:** The Elovich equation is general expressed as follow (Chien et al, 1980; Ketcha et al, 2012b):

$$\frac{dQ_t}{dt} = \alpha e^{-\beta Q_t} \quad (16)$$

where, α is the initial sorption rate (mg^{-1}.g.min^{-1}) and β is the desorption constant (g.mg^{-1}) during any one such experiment. The integrated and simplified form is:

$$Q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad (17)$$

Mass transfer kinetic model: the general equation of mass transfer kinetic model is as follows (Ketcha Mbadcam et al, 2011):

$$C_t = D_e k_0 t \quad (18)$$

where, C_0 and C_t are respectively the initial concentration and concentration of solute (mg/L) at an instant t (min), D is the mass transfer constant and K_0 (min^{-1}) the adsorption constant. The linearization of equation (18) permits us to obtain the following expression:

$$\ln(C_0 - C_t) = \ln D + k_0 t \quad (19)$$

Intraparticle diffusion kinetic model: the transportation of adsorbate from solution phase to the surface of the adsorbent particles may be controlled either by one or more steps such as: (i) film or external diffusion, (ii) pore diffusion, (iii) surface diffusion and (iv) adsorption on the pore surface, or a combination of more than one step (Kunquan et al, 2009). The general equation of intraparticle diffusion model is given by (Weber and Morris, 1963. Srivastava et al., 1989; Hameed and Daud, 2008; Idris et al, 2012b):

$$Q_t = k_{id} t^{1/2} + C \quad (20)$$

where, Q_t is the amount of pollutant adsorbed at time t, k_{id} ($mg.g^{-1}.min^{-1}$) is the intraparticle rate constant and C the intercept. In order to obtain parameters related to each kinetic model, experimental data have been tested with linear forms of these models. The straight-line plots are presented on Fig. 6 to 10, while the parametric constants for these models are given in Table 2. It can be noted that the adsorption of MB and phenol onto prepared activated carbon adequately follows respectively pseudo-second-order and mass transfer kinetics models from their correlation coefficient (R^2 = 1 and 0.9418)

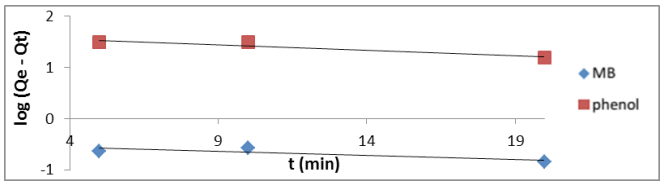

Figure 6: Linearized pseudo-first-order plots

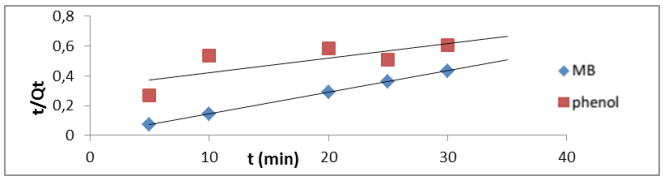

Figure 7: Linearized pseudo-second-order plots

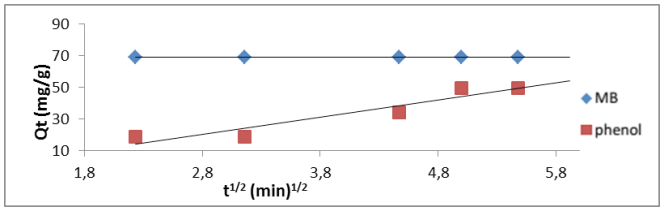

Figure 8: Linearized intraparticle diffusion plots

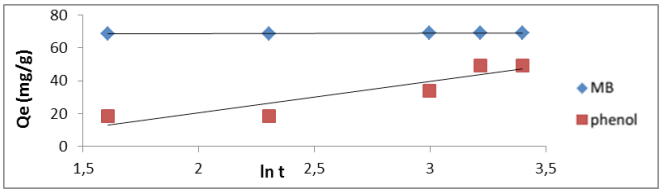

Figure 9: Linearized Elovich plots

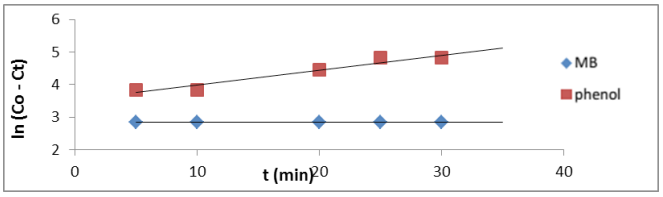

Figure 10: Linearized mass transfer equation plots

DISCUSSION

Characterisation of prepared activated carbon

The broad adsorption band at 3321 cm^{-1} is the characteristic stretching vibration of O-H for phenols, alcohols or carbonyls. The bands at 873, 802, and 752 cm^{-1} are due to plane deformation mode of C-H for different substituted benzene ring (Benadjemia *et al*, 2011). The band at 1574 cm^{-1} can be attributed to the stretching of carbonyl group (C=O), and the broad band at 1163 cm^{-1} represents the haloalkyl group (C-H) (Kunquan *et al*, 2009). The band at 1089.9 cm^{-1} is due to internal vibration of Si-O-Si (Maghri et al, 2012; Ravichandra et al, 2012).

The prepared activated carbon exhibit a low specific surface area of 2.0448 $m^2.g^{-1}$. This might be due to the activating reagent (KOH) because same precursor was used with same operating conditions, but at this time with $ZnCl_2$ as activation reagent which present a significant surface area of about 648 m^2/g (Ndi Nsami et al, 2013). The values of pore size and iodine number indicate that the prepared activated carbon consist of micropores and mesopores which are favourable for respective adsorption of MB and phenol.

Contact time

According to Fig.2, the first step might be due to the intraparticle transport of phenol from bulk solution to the external surface of the porous adsorbent and the second step the diffusion into the interior pore (Ranjan et al, 2009; Ndi Nsami et al, 2013). For MB, the amount adsorbed increases rapidly and reaches equilibrium after 5 minutes. This result showed that within this time, the adsorption sites were exhausted and the remaining vacant sites were difficult to be occupied by other molecules due to the repulsive forces between adsorbate present on solid and bulk phase (Tagne et al, 2013).

Adsorbent dose

The decrease in the quantity adsorbed can be due to the agglomeration/aggregation of adsorbent particles at higher masses, which limit the surface area available for the adsorbates and also the increase in the diffusional path length (Kunquan et al, 2009; Essomba et al, 2014).

pH

For the phenol adsorption (Fig. 4), at low pH value, the surface of activated carbon as well as phenol molecules gets protonated and with formation of positive charges on both adsorbate and adsorbent. This result leads to the reduction of phenol adsorption due to repulsive forces. With the increase of pH to 6, molecular form of phenol persist in the medium and surface protonation is minimum, leading to the enhancement of phenol adsorption and finally reaches its maximum (Jadhav and Vaujara, 2004). Significant decline in removal efficiency was for further increase in pH, which may be attributed to formation of phenolate anions and at the same time the presence of hydroxyl ions on the activated carbon prevents the uptake of phenolate ions (Ekpete et al, 2010). For the MB (Fig. 4), the amount adsorbed increases with an increase in pH value. This is probably due to the presence of delocalized π-electrons within the graphene layers which are described as Lewis basic site (electron donor) and which reacts with MB molecule which are positively charged (cationic dye) (Benadjemia et al, 2011).

Concentration

The adsorption capacity (Q_e) increased as initial MB concentration increased (Fig.5); showing that the initial concentration provides a powerful driving force to overcome the mass transfer resistance between the aqueous and solid phases (Tsai et al, 2006). For adsorption of phenol (Fig. 5), within 100 and 200 $mg.g^{-1}$ the amount adsorbed increases and beyond this interval, the amount adsorbed decreases with increase in concentration. The high sorption at the initial concentration may be due to an increased number of vacant sites on the activated carbon available at the initial stage. As the initial concentration increases there is a decrease in amount of phenol adsorbed due to the accumulation of phenol particles on the surface (Ekpete et al, 2010).

Isotherm

The results in table 2 show clearly that adsorption isotherms are in agreement with the Langmuir adsorption isotherm for both MB and phenol adsorption with higher values of correlation coefficient R^2 of 0.9875 and 0.8956 respectively. In addition, the mean sorption energy (E) which is given by the D-R adsorption isotherm is less than 8 $kJ.mol^{-1}$ (0.05 $kJ.mol^{-1}$) for phenol adsorption, indicating a physical adsorption. On the other hand, E = 12.9 $kJ.mol^{-1}$ for MB adsorption indicates the chemical process of adsorption (Ranjan et al, 2009). The values of R_L are 0.23 and 0.0003 for phenol and MB respectively, which indicates that the adsorption is favourable onto prepared activated carbon.

Kinetics

The high value of correlation coefficient implies that MB adsorption on activated carbon may occur through a chemical process involving the valence forces of shared or exchanged electrons (Ho, 2006). The kinetic of adsorption of phenol better fit the mass transfer kinetic model with high correlation coefficient, R^2 = 0.9418. In addition, the high value of the intraparticle rate constant (k_{id} =10.899 $mg.g^{-1}.min^{-1}$) indicates that the particle diffusion mechanism predominates in adsorption of phenol. Similar results have been reported by Idris et al 2012b, Idris et al, 2012.

CONCLUSION

The activated carbon prepared from cola nut shells was successfully employed as an adsorbent for the removal of MB and phenol in aqueous solution. The equilibrium data fitted well the Langmuir adsorption isotherms for both adsorbates. The values of R_L were found to be 0.23 and 0.0003 respectively for phenol and MB and confirmed that the prepared activated carbon is favorable for adsorption of both phenol and MB. The kinetics data of adsorption of phenol and MB follow respectively mass transfer and pseudo-second order model. These results indicated that the activated carbon prepared from cola nut shells could be used as low cost alternative adsorbents to commercial activated carbon in the removal of organic compounds such as phenol and MB from wastewater.

ACKNOWLEDGEMENT

The authors are grateful to Dr. Isaac Nongwe Beas, for recording the IR analysis; the Research Unit- Adsorption and Surface of the Applied Physical and Analytical Chemistry Laboratory of the University of Yaoundé I. The authors are also grateful to the scholars whose articles are cited and included in references of this manuscript, and grateful to authors, editors, and publishers of all the articles, journals and books from where the literature for this article has been reviewed and discussed.

REFERENCES

1. Alam Z. M., Muyibi A. S., Mansor F. M., Wahid R. 2006. Activated carbons derived from oil palm empty-fruit bunches: Application to environmental problems. *Journal of Environmental Sciences.* 19, 103-108.
2. Anagho Gabche s., Tchuifon Tchuifon D. R., Ndifor-Ang-

wafor N.G., Ndi Nsami J., Ketcha Mbadcam J., Nchare M. 2013. Nickel adsorption from aqueous solution onto kaolinite and metakaolinite: kinetic and equilibrium studies. *International Journal of chemistry*. 04, 1-14.
3. Benadjemia M., Millière L., Reinert L., Benderdouche N., Duclaux L. 2011. Preparation, characterization and Methylene Blue adsorption of phosphoric acid activated carbons from globe artichoke leaves. *Fuel Processing Technology*. 92, 1203-1212.
4. Ekpete O. A., Horsfall Jnr M., Tarowou T. 2010. Potential of fluted pumkin and commercial activated carbon for phenol removal in aqueous systems. *Journal of Engineering and Applied Science*. (5)9: 39-47.
5. Ekpete O. A., Spiff A. I., M. Horsfoll Jnr, Adowei P. 2012. Adsorption of phenol and chlorophenol in aqueous solution on a commercial activated in batch sorption systems. *Innovation in Science and Engineering*. 2, 72-78.
6. Essomba J. S., Ndi Nsami J., Belibi Belibi P. D., Tagne G. M., Ketcha Mbadcam J. 2014. Adsorption of cadmium(II) ions from aqueous solution onto kaolinite and metakaolinite. *Pure and Applied Chemical Sciences*. 2(11): 11- 30.
7. Guler C., Copur Y., Cihat T. 2007. The manufacture of particleboards using mixture of peanut hull (Arachis hypoqaeaL) and European Black pine (Pinus nigra Arnold) wood chips. *Bioresource Technology*. 99, 2893-2897.
8. Hameed B. H., Ahmed A. L., latiff K. N. A. 2007a. Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. *Dyes and Pigment*. 75, 143-149.
9. Hameed B. H., Din A. T. M., Ahmed A. L. 2007b. Adsorption of methylene blue onto bamboo-bossed activated carbon: kinetics and equilibrium studies. *Journal of Hazardous Materials*. 141, 819 – 825.
10. Hameed B.H., Daud F.B.M. 2008. Adsorption studies of basic dye on activated carbon derived from agricultural waste: Hevea brasiliensis seed coat. *Chemical Engineering Journal.* 139, 48-55.
11. Hanen N. and Abdelmottaleb O. 2013. Modeling of the Dynamics Adsorption of Phenol from an Aqueous Solution on Activated Carbon Produced from Olive Stones. *Chemical Engineering & Process Technology*. 4:3, 1-7.
12. Ho Yuh-Shan. 2006. Review of second-order models for adsorption systems. *Journal of Hazardous Materials*. 136, 681-689.
13. Idris S., Iyaka Y.A., Dauda B.E.N., Ndamitso M.M. and Umar M.T. 2012b. Kinetic study of utilizing groundnut shell as an adsorbent in removing chromium and nikel from dye effluent. *American Chemical Science Journal*. 2(1): 12-24.
14. Idris S., Ndamitso M. M., Iyaka Y. A., Muhammad E. B. 2012a. Sawdust as adsorbent for the removal of MB from aqueous solution adsorption and Equilibrium Studies. *Journal of Chemical Engineering*. 1(1): 12-24.
15. Isichei T. O. and Okieimen F. E. 2012. Adsorption of phenol onto water hyacinth activated carbon-kinetics and equilibrium studies. *Journal of Environmental Chemistry and Ecotoxicology*. 4(13): 234-241.
16. Jadhav A. N ., Vaujara A. k. 2004. Removal of phenol from waster using sawdust, polymerized sawdust and sawdust carbon. *Indian Journal of Chemical technology,* 11, 35-41.
17. Jaguaribe E. F., Medeiros L. L., Barreto M. C. S. and Araujo L. P. 2005. The performance of activated carbons from sugarcane bagasse, babassu, and coconut shells in removing residual chlorine. *Brazilian Journal of Chemical Engineering*. 22(1): 41-47.
18. Jeffery G. H., Bassett J., Mendham J., Denney R. C. (fifth editon), 1989. Vogel's textbook of quantitative chemical analysis. John Wiley and sons Inc., 605 Third Avenue, New York N Y 10158, 408 - 409.
19. Karabacakoğlu B., Tümsek F., Demiral H., Demiral I. 2008. Liquid Phase Adsorption of Phenol by Activated Carbon Derived From Hazelnut Bagasse. *J. Int. Environmental Application & Science*. 3(5): 373-380.
20. Ketcha Mbadcam J., Dina Joh D. D., H.M. Ngomo and Ndi N.J. 2012a. Preparation and Characterization of Activated Carbons Obtained from Maize Cobs by Zinc Chloride Activation. *American Chemical Science Journal*. 2(4): 136-160.
21. Ketcha Mbadcam J., Dongmo S. and Dinka'a Ndaghu D. 2012b. Kinetic and thermodynamic Studies of the Adsorption of Ni(II) ions from Aqueous solutions by Smectite Clay from Sagba-Cameroun. *International Journal of Current Research*. 4(5): 162-167.
22. Ketcha Mbadcam. J., Anagho Gabche S., Ndi Nsami. J., kammegne A.M. 2011. Kinetic and equilibrium studies of the adsorption of lead (II) ions from aqueous solution onto Cameroon clays: kaolinote and smectite. *Journal of Environmental Chemistry and Ecotoxicology*. 3(11): 290-297.
23. Kobya M., Demirbas E., Senturk E., Ince M. 2005. Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. *Bioresource Technology*. 96, 1518-1521.
24. Kunquan L., Zheng Z., Xingfa H., Guohua Z., Jingwei F., Jibiao Z. 2009. Equilibrium, kinetic and thermodynamic studies on the adsorption of 2-nitroaniline onto activated carbon prepared from cotton stalk fiber. *Journal of Hazardous Materials*. 166, 213-220.
25. Maghri I., Kenz A., Elkouali M., Tanane O., Talbi M. 2012. Textile Dyes removal from Industrial Waste Water by Mytilus Edulis Shells. *Journal of Materials Environmental Science*. 3(1): 121-136.
26. Moraitopoules I., Ioannou Z., Simitzis J. 2009. Adsorption of phenol, 3 – nitrophenol and Dyes from aqueous solution onto and activated carbon column under semi – Batch and Continuous operation. *World Academy of science, Engineering and technology*. 34, 218–222.
27. Ndi Nsami J., Ketcha Mbadcam J., Anagho Ngabche S., Ghogomu Numboniu J., Belibi Belibi P. D. 2014. Physical and chemical characteristics of activated carbon prepared by pyrolysis of chemically treated Cola nut (cola acuminata) Shells wastes and its ability to adsorb organics. *International Journal of Advanced Chemical Technologie*. 3(1): 1 – 13.
28. Ndi Nsami J., Ketcha Mbadcam. J. 2013. "The adsorption efficiency of chemically prepared activated carbon from cola nut shells by $ZnCl_2$ on methylene blue". *Hindawi Publishing Corporation Journal of Chemistry*, 1-7.
29. Ranjan D., Talat M., Hasan S.H. 2009. Biosorption of arsenic from aqueous solution using agricultural residue 'rice polish'. *Journal of Hazardous Materials*, 166, 1050-1059.
30. Ranjan D., Talat M., Hasan S.H. 2009. Biosorption of arsenic from aqueous solution using agricultural residue rice polish. *Journal of hazardous materials*. 166, 1050-1059.
31. Ravichandra P., Farzana H. M., and Meenakshi S. 2012. Sorption equilibrium and kinetic studies of Direct Yellow 12 using carbon prepared from bagasse, rice husk and tex-

tile waste cloth. *Indian Journal of Chemical Technology*, 19, 103-110.
32. Reddy S. B., Krishna V., and Ravindhranath K. 2012. Removal of methylene blue dye from waste waters using new bio-sorbents derived from *Annona squamosa* and *Azadiracta indica* plants. *Journal of Chemical and Pharmaceutical Research*. 4(11): 4682-4694
33. Shen J., Xie Y., Zhou Y. 2009. Adsorption of methylene blue from aqueous solution on pyrophyllite. *Applied Clay Science*. 46, 422-424.
34. Tagne G. M., Ndi Nsami J., Ketcha Mbadcam J., 2013. Adsorption of copper ions from aqueous solution onto synthetic geothite and two natural aviable red soils from Yaoundé-Cameroon. *British Biotechnology Journal*. 3(3): 221 – 235
35. Tsai W. T., Lai C. W., Su T. Y. 2006. Adsorption of bisphenol-A from aqueous solution onto minerals and carbon adsorbents. *Journal of Hazardous Materials*. 134, 169-175.
36. Tsai W.T., Chang C.Y., Wang S.Y., Chang C.F., Chien S.F., Sun H.F. 2001. Cleaner production of carbon adsorbents by utilizing agricultural waste corn cob, *Resources, Conservation and Recycling*, 32, 43-53.
37. Varghese S., Vinod V. P., Anirudhan T. S. 2004. Activated carbons derived from oil palm empty-fruit bunches: Application to environmental problems. *Indian Journal of Chemical Technology*. 11, 825-833.
38. Wu F.C., Tseng R.L., Juang R.S. 2005. Preparation of highly micro porous carbons from fir wood by KOH activation for adsorption of dyes and phenol from water. *Separation and Purification Technology*. 47, 10-19.
39. Yahaya E. M. K. N., Latiff M. P. F. M., Abustan I., Bello S. O., Ahmad M. A. 2011. Adsorptive Removal of Cu (II) Using Activated Carbon Prepared From Rice Husk by $ZnCl_2$ Activation and Subsequent Gasification with CO_2. *International Journal of Engineering & Technology*. 11(2): 164-168.
40. Kouotou D., Ngomo Manga H., Baçaoui A., Yaacoubi A. and Ketcha Mbadcam J. 2013. Physicochemical Activation of Oil Palm Shells using Response surface Methodology: Optimization of Activated Carbons Preparation". International Journal of Current Research, 5(3), 431-438.
41. Kouotou D., Horace Ngomo Manga, Abdelaziz Baçaoui, Abdelrani Yaacoubi and Ketcha Mbadcam J. 2013. Optimization of Activated Carbons prepared by H_3PO_4 and Steam Activation of Oil Palm Shells, *Journal of Chemistry*, article ID 654343,10.
42. Ketcha Mbadcam J., Ngomo Manga H., Kouotou D., Ngamou Tchoua P. H.., "Kinetic and Equilibrium Studies of the Adsorption of Nitrate Ions in Aqueous Solutions by Activated Carbons and Zeolite". *Research Journal of Chemical Environ*ment, 11(3), 47, 2007.
43. Largregren S. About the Theory of so called Adsorption of Soluble Substances, *Ksver verterskapsakard Handl* 24, 1-6, 1898.
44. Ho Y.S., Mckay G. D., Wase A.J. and Foster C.F. 2000. Study of the Divalent Metal Ions on to Peat. *Adsorption Science and Technology*, 18, 635-650.
45. Chien S. H. and Clayton W. R. 1980. Application of Elovich Equation to the Kinetics of Phosphate Release and Sorption on Soils, *Soil Science Society of American Journal*, 44, 265-268.
46. Weber W. J. and Morris J. C. 1963. Kinetics of Adsorption on Carbon from Solution, *J. Sanit. Eng. Div. American Society of Civil Engineering*, 89, 31-60.