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Adsorption of phenol from aqueous solutions onto natural and thermally-modified kaolinitic materials

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ABSTRACT

Phenol removal from aqueous solutions by kaolinite (KAO) and metakaolinite (MET) have been carried out at 25 °C in batch mode to evaluate the effects of parameters such as pH, initial phenol concentration and adsorbent mass on the extent of adsorption. It was observed that phenol uptake increased with increases in adsorbent concentration at maximum pH of 2 and equilibrium time of 40 minutes for both KAO and MET. Results showed that pseudo second-order kinetic model best describes the chemisorption of phenol from aqueous solutions onto the two clay samples. The low correlation coefficient of the intraparticle diffusion model proves that pore diffusion plays little or no significant role in the adsorption of phenol onto KAO and MET. Also, from adsorption isotherm analysis, only the Temkin equation modeled best the adsorption process of phenol from aqueous solutions onto MET while the Freundlich and Temkin models best described the adsorption of phenol onto KAO. Maximum adsorption capacity for KAO and MET were 1.71 and 5.82 mg/g respectively through Langmuir model equation. It can be inferred from experimental results and modeled parameters that clay samples are not very effective for the removal of phenol from aqueous solution.
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Keywords: Environment, clays, organic pollutants, Kinetic models, Isotherm models.

INTRODUCTION

Pollution by phenols is an important environmental issue. Phenols are common pollutants in wastewater generated from oil, gasoline, coal, paper, petrochemicals, pharmaceuticals, pesticides and dye manufacturing industries (Ekpete et al., 2010). They are considered as one of the primary pollutants in wastewater because they are harmful to organisms even at low concentrations and many of them have been classified as hazardous pollutants because of their potential hazards to human health. Chronic toxic effects due to phenolic compounds reported in humans include vomiting, difficulty in swallowing, anorexia, liver and kidney damage, headache, fainting and other mental disturbance (Ekpete et al.,

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2012). The low volatility of phenol and its affinity to water make oral consumption of contaminated water the greatest risk to humans (Mostafa et al., 1989; Prpich and Daugulis, 2005). This aromatic compound is water soluble and highly mobile and as such, waste waters generated from industrial activities contain high concentrations of phenolic compounds (Dursun and Kalayei, 2005) which eventually reach down to streams, rivers, lakes and soils. Their ubiquity represents a serious ecological issue that calls for global attention (Sofia, 2005). In the past several decades, extensive research has been conducted to develop innovative and promising adsorbent material for dealing with the treatment of contaminated industrial effluents. There is a growing interest in cost effective innovative materials and methods that will be useful in the treatment of industrial waste streams (Chen and Zhao, 2010; Theivarasu et al., 2011). Many agricultural by-products that are available at little or no cost have been reported to be capable of removing substantial amounts of phenol derivatives from aqueous solutions (Okieimen et al., 2007; Uddin et al., 2007). In compliance with stipulated norms, many depollution techniques such as flocculation, chemical precipitation, solvent extraction, membrane processes (ion exchange or electrodialysis, reverse osmosis etc) and adsorption are used for wastewater treatment especially in the removal of organic compounds (Achour and Youcef., 2003). The adsorption technique is most convivial and economically viable as the adsorbent is easily regenerated (Ketcha and Bougo, 2010).The adsorptive properties of clay for the removal of the pollutants are well documented (Ghogomu et al., 2013). Most currently used adsorbents for phenolic compound removal include organic materials such as marine algae (Najua et al., 2008) activated carbon prepared from green algae and elais guineensis (Ola, 2007); malachite green (Rajesh et al., 2010) or inorganic such as goethite (Grossl et al., 1994), layered double hydroxides (Goswamee et al., 1998), laterite (Maji et al., 2007), used tyres and sawdust (Hamadi et al., 2001), activated carbon (Han et al., 2000), smectite (Ketcha et al., 2009), zeolite (Tahir et al., 1998), hydrated Iron hydroxyde and clay minerals such as kaolinites (Lazaridis et al., 2001). After testing for the adsorption of some inorganic pollutants such as Lead (Ghogomu et al., 2013) and mercury (Anagho et al., 2013) by Kaolinite and methakaolinite we envisage in this study, the adsorption of an organic pollutant (phenol with aromatic properties) onto two adsorbent materials viz Natural and thermally-modified Kaolinite.

MATERIALS AND METHODS

Raw samples of Kaolinite (KAO) made up of clay materials were collected locally from the south region of Cameroon. Metakaolinite (MET) was obtained from kaolinite by thermal treatment (calcinations). Analysis of the chemical composition of KAO and MET was by x-ray fluorescence.

Preparation of adsorbent

In order to enrich the collected clay samples in kaolinite before use, samples were soaked inside distilled water for 24 h, then washed in a 100 micron sieve immediately afterwards and were finally sun-dried. This procedure was repeated once more but using a sieve of 80 microns. The kaolinitic product obtained ($Al_2Si_2O_5(OH)_4$) was oven-dried at 110 °C for 24 h. After drying, 500 g samples of the kaolinite were weighed and grounded in a mortar with pestle to fine powder and sieved to 80 micron size. Metakaolinite was obtained from kaolinite by dehydroxylation in a carbolite furnace maintained at 700 °C for 24 h according to equation 1 below.

$$Al_2O_3.2SiO_3.2H_2O \mapsto Al_2O_3.2SiO_3 + 2H_2O \quad \text{….. (1)}$$

The carbonized material was taken out, grounded to fine powder, then sieved to 80 micron size and was finally stored in vacuum desiccators.

Preparation of solutions

Stock solution of phenol

(C_6H_5OH, 99.5%, Merck-Aldrich) was prepared by dissolving 1.0 g of the salt in 1 Liter of distilled water to give a concentration of 1000 ppm. Serial dilutions for working solutions were made by diluting the stock solution in accurate proportions.

pH adjustment solutions

pH adjustment solutions were prepared using hydrochloric acid (0.1M, 60%, Riedel-de-Haen) and sodium hydroxide (0.1 M of 98%, Fluka) solutions respectively.

Batch adsorption experiments

Equilibrium and kinetic adsorption experiments were carried out in a temperature controlled batch adsorption reactor maintained at 25 ^{o}C. All the experiments (except the study of the effect of pH) were carried out at a pH of 7.5. For each experiment (except otherwise stated), 0.2 g of adsorbent were measured and put into a 250-mL conical flask containing 25 mL of the phenol solution at the desired concentration that ranged between 20 and 160 ppm in this study. After stirring the solution for a predetermined time interval (5-60 minutes) with a magnetic agitator, samples were then filtered, thus separating the solid/adsorbent from the liquid/solution phase. The filtered solution was analyzed spectrometrically to determine the concentration of the residual phenol using a UV-Visible spectrophotometer (CORNING6259) at λ_{max} = 270 nm. Adsorption data obtained from equilibrium studies (contact time and initiation concentration effects) were employed in the kinetic studies and the applicability of different adsorption isotherms to phenol. The percentage removal efficiency of the adsorbents (%R), which is the ratio between sorption capacity at time *t* and the sorption capacity at equilibrium are calculated as follows:

% (R) adsorption = $100(C_o-C_t)/C_o$

Q_t(mg/g) = $(C_o-C_t)V/m$

(2) Q_e (mg/g) = $(C_o-C_e)V/m$

Where C_o(mg/L) and C_t (mg/L) are the liquid-phase concentrations of solute (adsorbate) at the origin and at a given time *t*, respectively. C_e(mg/L) is the equilibrium concentration of phenol, V(L) is the volume of the solution while m(g) is the mass (m) of the adsorbent.

Kinetic models

Adsorption kinetics describes the relationship between the rate of solute uptake and adsorption time. In order to verify the adsorption kinetic models, the pseudo-first-order, the pseudo-second-order, the Elovich and intraparticle diffusion models were applied to the experimental raw data.

Pseudo first-order model

This model is based on the assumption that the adsorption rate is proportional to the number of available sites (Augustine et al., 2007) and is calculated through the following equation:

$dQ_t/dt=K_f(Q_e-Q_t)$ (3)

Where Q_t and Q_e (mg/g) are the amounts of adsorbate retained per unit mass of adsorbent at given time and at equilibrium respectively. K_f (min^{-1}) is the rate constant of the adsorption process. By integrating between t = 0 and t = t (corresponding to Q_t=0 and Q_t = Q_t), we obtain the following:

$\ln(Q_e-Q_t)=\ln Q_e-K_f t$ (4) Linear plots of $\ln(Q_e-Q_t)$ versus t were carried out in order to evaluate this kinetic model and to determine Q_e and the rate constant from the intercept and slope respectively.

Pseudo second-order model

It is based on the assumption that adsorption rate is proportional to the square of the number of unoccupied sites (Ho and Mckay, 1998):

$dQ_t/dt = Ks(Q_e-Q_t)^2$ (5)

where Ks ($mg.g^{-1}.min^{-1}$) is the rate constant. By integrating between t=0 and t=t (corresponding to Q_t=0 and Q_t =Q_t), we obtain the following:

$t/Q_t = 1/KsQ_e^2 + t/Q_e$ (6)

The parameters Ks and Q_e can be calculated from the intercepts and the slope of the graph of t/Q_t versus t.

Elovich model

Elovich equation is a rate equation based on the adsorption capacity Q_t (mg/g), an equation that can be expressed as (Ketcha and Bougo, 2010):

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

where α= initial adsorption rate ($mg.g^{-1}.min^{-1}$) and β is related to the extent of surface coverage and activation energy for chemisorption (g/mg).

By integrating between t=0 and t=t (corresponding to Q_t=0 and Q_t =Q_t), we obtain the following after some simplifications:

$Q_t = \ln(\alpha\beta)/\beta + \ln t/\beta$ (8)

The value of the constants can be obtained from the slope and intercepts of a plot of Q_t versus log t.

Intra-particle diffusion model

The intra-particle diffusion model equation can be written as follows (Ghogomu et al., 2013):

$Q_t = K_{id}\, t^{1/2} + C$, (9)

where K_{id} is the intra-particle rate constant ($mg.g^{-1}.min^{-1/2}$) and C is the intercept. By plotting Q_t ($mg.g^{-1}$) versus $t^{1/2}$ one should obtain a linear graph if the intra-particle diffusion is involved in the adsorption process. If the straight line passes through the origin, the intra-particle diffusion is the rate limiting step.

Adsorption models

There are a number of sorption models developed to describe the adsorption mechanism and to fit the experimental adsorption data. Three models were used in this study in investigating the mechanism of phenol adsorption on our clay samples: the Langmuir, Freundlich and Temkin isotherms equations respectively.

The Langmuir isotherm

The mathematical expression of the Langmuir isotherm can be written as (Ghogomu et al., 2013):

$Q/Q_m = KC_e/(1+KC_e)$ (10)

In this equation, C_e is the bulk equilibrium concentration of adsorbate in solution, K is an affinity constant, Q is the amount of the adsorbate at equilibrium concentration C_e and Q_m is the amount necessary for monolayer surface coverage by adsorbate. In this adsorption isotherm, an assumption is made that the energy of adsorption is constant at all concentrations up to the full coverage of the surface. The Langmuir equation can be rewritten in linear form as:

$C_e/Q = 1/K.Q_m + C_e/Q_m$ (11)

Equation (11) implies that a graph of C_e/Q versus C_e should give a straight line.

Freundlich isotherm

Another type of equation which has been used in this work to fit the adsorption data is the Freundlich equation, which can be written as (Ketcha and Bougo, 2010):

$Q = K_d Ce^{1/n}$ (12)

In this equation, Q is the amount adsorbed at the surface; Ce is the equilibrium concentration of adsorbate in solution, K_d is the distribution coefficient and n is a correction factor related to the heterogeneity of the surface. Taking the logarithm of either sides of this equation, it can be rewritten as:

$\ln Q = 1/n \ln C_e + \ln Kd$ (13)

From which we see that a plot of ln Q versus ln C_e should give rise to a straight line with a slope of 1/n and intercept equal to $\ln K_d$ if the adsorption follows a Freundlich isotherm. Another type of equation which has been applied to our adsorption data is the:

Temkin isotherm

It is expressed in linear form by the following relationship between the amount adsorbed and concentration in solution (Ghogomu et al., 2013):

$Q_e = B(\ln K_T + \ln C_e)$ (14)

where B =RT/b is related to the heat of adsorption, T is the absolute temperature, R is the universal gas constant. B indicates the

adsorption potential of the adsorbent and K_T is the equilibrium binding constant. Similar to the Freundlich equation, the Temkin model takes into account the heterogeneity of the surface.

RESULTS AND DISCUSSION

Characterization of adsorbent

Chemical composition of materials

Metakaolinite (MET) was obtained from kaolinite by thermal activation (calcination). Analysis of the chemical composition of KAO and MET by X-ray fluorescence showed the following results in percentages for KAO: weight loss (5.05); SiO_2(49.52); Al_2O_3(32.04); Na_2O (0.00); TiO_2(0.9864); Fe_2O_3(0.7526); K_2O(0.689); MgO(0.125); CaO(0.0406); SO_3(0.037); P_2O_5(0.034); NiO(0.0126); Cr_2O_3(0.011); CuO(0.0078); ZnO(0.0057); Ga_2O_3(0.005); Rb_2O(0.0047) for a total of 100.0014%.

And for MET*:* weight loss (5.05); SiO_2(46.99); Al_2O_3(34.66); Na_2O(10.55); TiO_2(0.941); Fe_2O_3(0.7889); K_2O(0.685); MgO(0.156); CaO(0.0606); SO_3(0.04); P_2O_5(0.03); NiO(0.0121); Cr_2O_3(0.01); CuO(0.0077); ZnO(0.006); Ga_2O_3(0.004); Rb_2O(0.0045) for a total of 99,9958%.

FT-IR spectroscopy

FT-IR spectroscopic measurements were carried out to characterize the Kaolinite (KAO) and metakaolinite (MET) samples and results have been illustrated in Figures 1 and 2 below.

The analysis of the first spectrum (Figure 1) show absorption bands at 3693 cm^{-1}; 3656 cm^{-1}; and 3620 cm^{-1} which corresponds to stretching vibrations of the hydroxyl (OH) of KAO, and average band at 1110 cm^{-1} by the Si-O functional group and at 1000, 1025, 402 cm^{-1} for symmetric and asymmetric vibration of the Si-O-Si group. We also perceived a small band at 908 cm^{-1} for the deformation of the Al-OH bond of the KAO. Also present is another band between 790-748 cm^{-1} which are translational vibration bands for Si-O-Al and finally a Si-O-Si characteristic band of KAO at 666 cm^{-1} is visible (Ghogomu et al., 2013). The result obtained here imply the existence of repulsive electrostatic interactions between the OH functional groups of KAO and that of phenol with the effect of reducing the adsorption capacity at the surface of the adsorbents. We also notice the hydrophobic character of the adsorbents due to the presence of siloxane groups (Si-O-Si) (Djebbar et al., 2012) which is in conformity with our results on the adsorption capacity of the sorbent materials vis-à-vis others from the literature cited below in the text (Table 1).

We observe on the second spectrum (Figure 2) that all the vibrational bands due to the hydroxyl group (OH) are absent and only characteristic absorption bands for the Si-O at 1042 cm^{-1}, for Si-O-Al at 787 cm^{-1} and 542 cm^{-1} (Ghogomu et al., 2013) respectively are present.

Pore size distribution by the Barret-Joyner-Halenda method (BJH)

The BJH method establishes the link between thermodynamic, sorption isotherm, geometrical data, intrinsic properties of the solid and the pore size distribution. Classically, this method uses nitrogen at 77 K as adsorbate gas. The results of this distribution, adsorption and desorption isotherms (BET) obtained on metakaolinite only are presented on Table 1 and Figure 3 below.

This isotherm (Figure 3) is reversible and convex with relative pressure axis corresponding to type-3 hysteresis according to the nomenclature of International Union of Pure and Applied Chemistry (IUPAC). This type of hysteresis is often encountered with non-porous or macroporous materials characterized by weak affinity between adsorbent and adsorbate and within molecules as well.

Effect of contact time

The influence of contact time on the

adsorption of phenol from aqueous solution onto the two clay samples has been presented on Figure 4 below. These results were obtained at pH=8.5 with mixtures of 25 mL of phenol solution (at 100 mg/L) with 0.10 g of the different adsorbents. Sorption equilibrium time was observed after 40 minutes for both KAO and MET for an equilibrium time range of 5-60 minutes. From this figure we observe that for a given time, phenol removal by MET is more effective than by KAO. It is also inferred here that adsorption takes place in two steps. The first step, between 0-10 minutes, is attributable to the presence of free adsorption sites at the surface of the adsorbent. The progressive occupation of these sites noticed as phenol molecules diffuses through the adsorbent pores comes to a halt followed by a saturation controlled by sorption equilibrium time, marking the second step. After the attainment of equilibrium, the quantity of solute removed from solution doesn't change significantly indicating that 40 minutes is sufficient time for equilibrium to be reached. From literature, Kannam (1998) working with tea powder and saw dust to remove phenol from its aqueous solutions obtained 180 minutes as contact time. Also, Singh et al. (1994) reported 120 minutes as equilibrium time for the removal of phenol from aqueous solutions by using impregnated ash. Qadeer and Rehan (2002) on their part, working with commercial activated carbon in the removal of phenol found that 5 minutes were required for the attainment of equilibrium. Comparing our results with similar works in the literature (Table 2, Figures 4 and 5), we notice that our clay samples are more efficient in the removal of phenol from aqueous solutions.

Effect of adsorbent dosage

The removal of phenol from aqueous solutions by the two clay samples was studied by varying the masses of the adsorbent from 0.1 to 0.7 g while maintaining the other parameters constant. The percentage removal of phenol as a function of adsorbent mass has been illustrated in Figure 5. This figure shows that the percentage adsorption of phenol increases with adsorbent dose up till 0.1 g (R=45% for MET and 90% for KAO respectively) and stabilizes more or less thereafter where no significant increase is noticed. At this portion of the curves, adsorption is marginalized and becomes pretty constant (Ekpete et al., 2010). Adsorbent dosage has a direct effect on the adsorbate removal because of increases in adsorbent surface and the adsorption sites.

Effect of initial concentration

Figure 6 shows that the quantity of phenol taken up at equilibrium increases with initial concentration of phenol in the aqueous solutions used. Similar results were obtained by Ghogomu et al. (2013). This result is attributed to the fact that KAO and MET adsorb very little at low adsorbate concentrations. The increase in the quantity adsorbed with initial concentration of phenol increases the collisions between phenol molecules and adsorption sites. It can be noticed from this result that the quantity adsorbed remains constant (for concentrations greater than 200 mg/L) as the adsorption sites become saturated while the exchange sites are filled. The conclusion here is that surface saturation at equilibrium depends on the initial concentration of the adsorbate solution.

Effect of pH

The effect of pH on phenol uptake from aqueous solutions has been studied within a pH range of 2-12. pH adjustments were done by addition of either 0.1 M HCl or 0.1 M NaOH to 100 mg/L solution of phenol. For KAO, the quantity of phenol adsorbed diminishes slightly with pH before reaching a plateau and we conclude that the adsorbed quantity may be pH independent. As concerns MET, this quantity is almost constant at the beginning and suddenly decreases with pH. This sudden decrease in pH corresponds to the formation of phenolate ions.

Phenol as a weak acid will undergo less adsorption at higher pH values because of the repulsive forces prevailing at higher pH values. Adsorption takes place only when the strong chemical bond between water and the adsorbate is broken. In addition, the adsorption force decreases as the repulsion between the adsorbent surface and the dissociated adsorbate increases. Also, we observe that the hydrophobic character of the materials is reinforced at low pH values thus rendering their surface less active.

Adsorption kinetics

Generally, kinetic studies of adsorption processes provide pieces of information on the adsorption mechanism, mode and speed of mass transfer from the liquid phase to the solid phase. Many kinetic models abound in the literature. (Ho and McKay, 1999). They are governed by parameters such as concentration, mass, pH, working conditions, etc. In this work, kinetics of phenol adsorption have been studied according to four principal models: Pseudo-first-order, Pseudo-second-order, Elovich kinetic model and Intra-particle diffusion model. Characteristic parameters have been obtained from linear plots of each model. Figure 8 shows the graph for the linear plot of quantity adsorbed versus time for the pseudo second-order model (obtained for the different clay samples) while Table 3 displays the different values of the parameters for the four different models. From this table, we infer that the adsorption of phenol onto the clay samples follow pseudo second-order kinetic model (R^2 = 0.994 for KAO and R^2 = 0.998 for MET) and as a consequence classified as a chemisorption process. The different behaviors of the four kinetic samples to the adsorbents are attributed to structural differences between them (Rajesh et al., 2010). Results from intra-particule diffusion model show that the adsorption process is governed by external diffusion (Xiu-yan, 2010).

Adsorption isotherms

Equilibrium studies of the adsorption of phenol from aqueous solutions by KAO and MET have been carried out according to three isotherm models: Langmuir, Freundlich and Temkin adsorption isotherms. The summary of the constants governing these isotherm models have been presented on Table 4. From this table we observe a low maximum adsorption capacity for KAO and MET as 1.71 and 5.82 mg/g respectively from Langmuir isotherm model (r^2=0.8937 for KAO and r^2=0.0294). Also, we observed from these results that while Freundlich (r^2=0.9478) and Temkin (r^2=0.9632) isotherm models best describe the adsorption phenomenon of phenol onto KAO, the Temkin (r^2=0.9423) model only suits phenol adsorption for MET. This is supported by the values $0<1/n<1$ and a positive value for the adsorption energy, B_T, for KAO and MET, indicative of the endothermic nature of the adsorption process (Augustine et al., 2007). The compliance of the Temkin model is a testimony of adsorption of phenol from aqueous solution onto the clay samples and consequently explains the weak interaction at the adsorbent surface. We also notice here that B_T for KAO is less than 8kJ/mol which means that interactions between adsorbent and adsorbate are weak and that the adsorption mechanism put into place is characterized by ion exchange. B_T is greater than 8 kJ/mol for MET so the interaction between the adsorbate and adsorbent is strong and the mechanism put into play is characterized by external diffusion of the adsorbate from the surface films to the adsorbent. On the basis of experimental results and the isotherm model parameters (Langmuir, Freundlich and Tempkin), it can be inferred that the multilayer sorption of phenol from aqueous solution onto heterogeneous surface of clay is feasible.

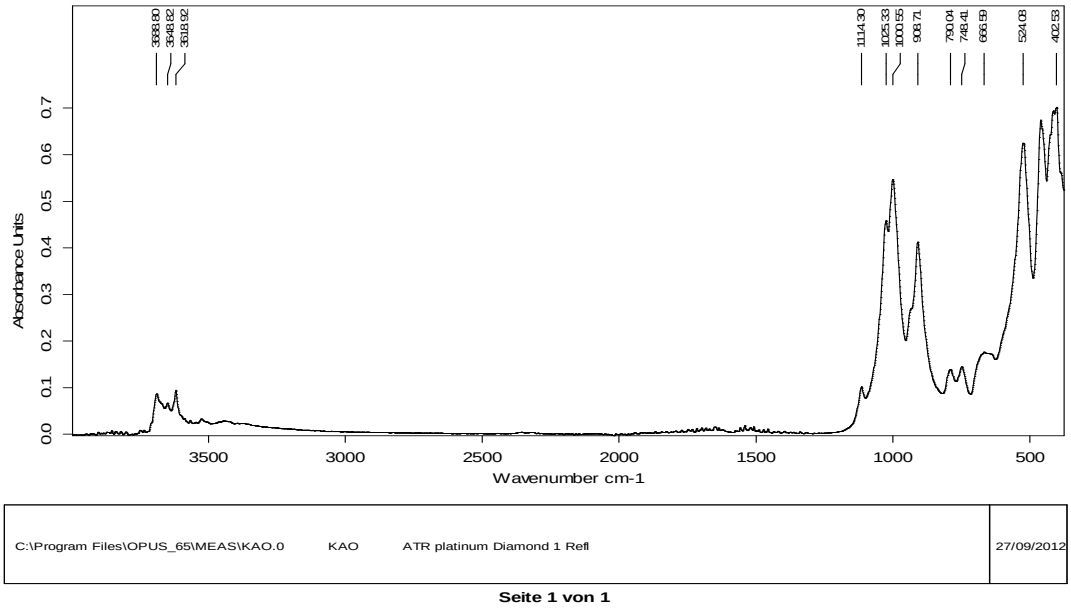

Figure 1: FT-IR spectrum of Kaolinite on platinium in KBr matrix.

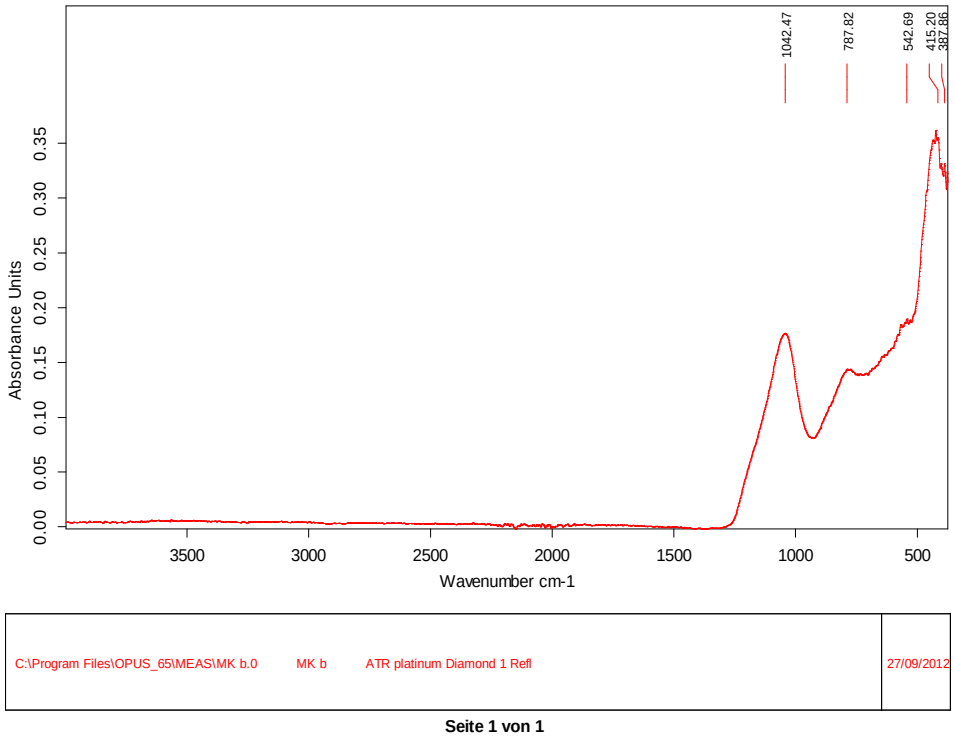

Figure 2: FT-IR spectrum of metakaolinite on platinium in KBr matrix.

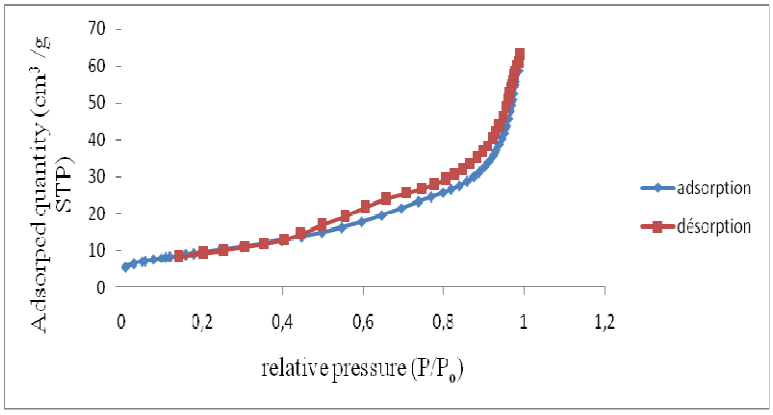

Figure 3: BET adsorption and desorption isotherm with nitrogen on metakaolinite at 77 K.

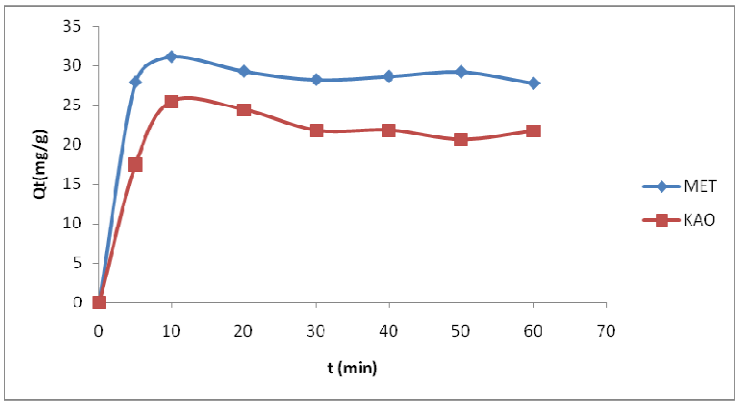

Figure 4: Influence of contact time on the sorption of phenol from aqueous solutions. V_o=25 mL; C_o = 100 mg/L phenol solution; m_o =0.1 g for KAO and MET; pH=8.5; T=298 K).

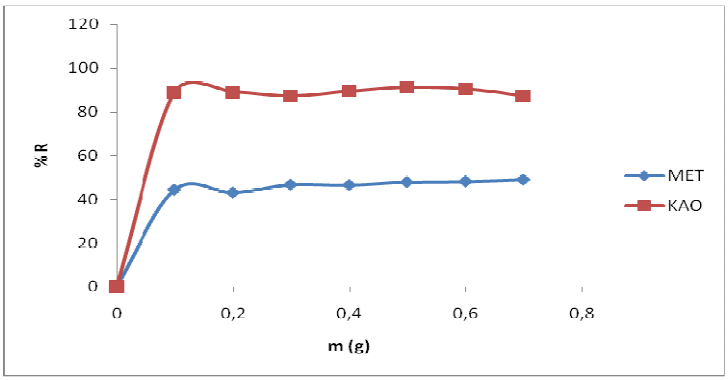

Figure 5: Influence of adsorbent dose on the sorption of phenol from aqueous solutions. (V_o=25 mL; C_o=100 mg/L phenol solution; pH=8.5; *t*eq = 40 min; T=298 K).

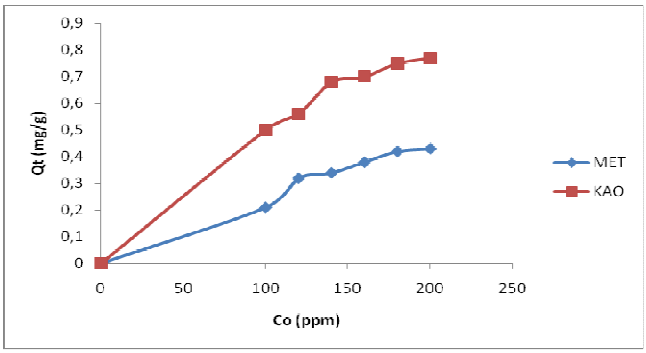

Figure 6: Influence of initial concentration on the sorption of phenol from aqueous solutions. (V_o=25 mL; C_o=100 mg/L phenol solution; pH=2; *t*eq=40 mins ; 0.2g KAO and MET; T=298 K).

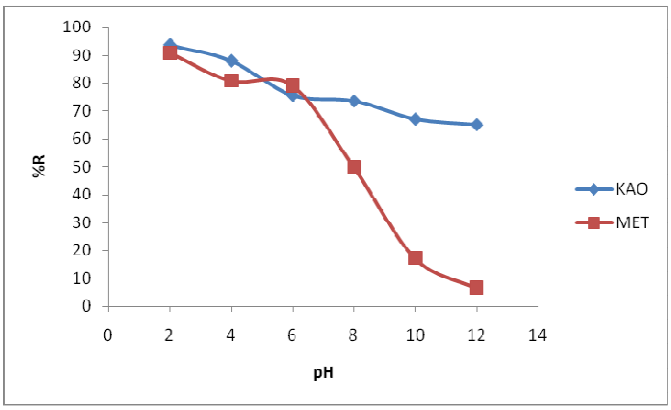

Figure 7: Influence of pH on the sorption of phenol from aqueous solutions. (V_o=25 mL; C_o=100 mg/L phenol solution; *t*eq=40 min; 0.2g KAO and MET ; T=298 K).

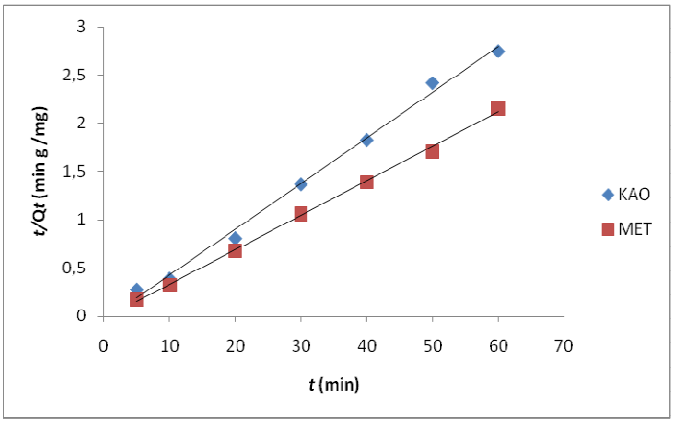

Figure 8: Linear plots of pseudo second–order kinetic model at 100mg/L and at pH=8.

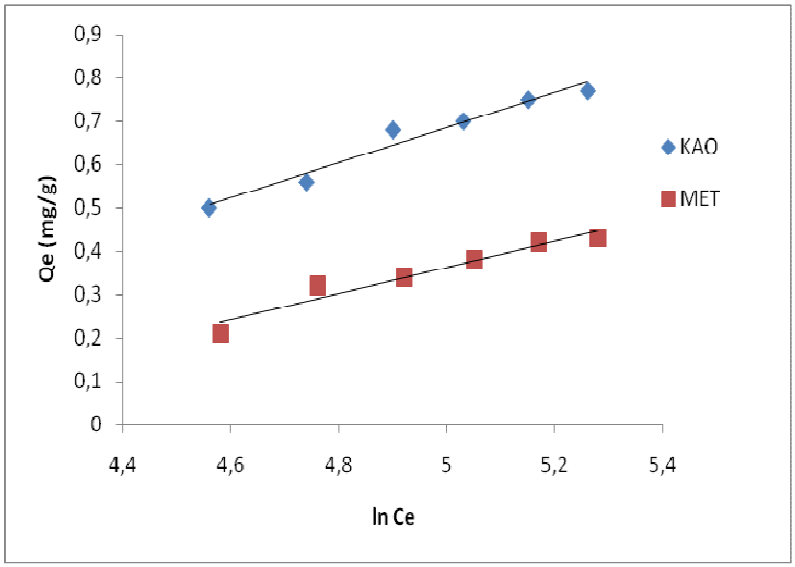

Figure 9: Linear plots of the Temkin isotherm model.

Table 1: Porosity Characteristic of Metakaolinite.

Sample	BET Specific surface area (m^2/g)	Average pore size (nm)	Average pore diameter (nm)	Total pore volume (cm^3/g)	Hysterisis type
Metakaolinite	33.8331	11.05476	9.9178	0.093504	III

Table 2. Comparison of the quantity of Phenol Adsorbed by different adsorbents.

Author	Adsorbent	Maximum adsorption capacity
Chen et al., 2011	clay-solidified grouting curtain	8.4 mg/g
Sofia et al., 2005	Porous clay Heterostructure	14.5 mg/g
Djebbar et al., 2012	Natural Clay	15.0 mg/g
This Work	KAO	25.48 mg/g
This Work	MET	31.1 mg/g

Table 3: Results of linear plots for the adsorption of phenol by KAO and MET.

Adsorbent		**KAO**	**MET**
C_o (mg/L)		**100 ppm**	**100 ppm**
Pseudo-first-order	K_1(min^{-1})	0.0461	-0.0041
	Q_e(mg/g)	1.78	0.57
	r^2	0.2352	0.0907
Pseudo-second-order	K_2(g/min.mg)	-0.048	-0.046
	Q_e(mg/g)	21.14	28.01
	r^2	0.994	0.998
Elovich kinetic model	α(mg/g min)	$1.36x10^{19}$	$-1.05x10^{-42}$
	β(g/mg)	2.19	-3.20
	r^2	0.0253	0.0605
Intra-particle diffusion model	K_d(mg/gmin$^{1/2}$)	0.0464	-0.1869
	C(mg/g)	21.663	29.835
	r^2	0.0013	0.1084

Table 4: Summary of the different isotherm plots of the adsorption of phenol by KAO and MET.

Model	**Langmuir**			**Freundlich**			**Temkin**		
Parameter	**K_L(L/mg)**	**Q_m(mg/g)**	**r^2**	**K_F(L/mg)**	**1/n**	**r^2**	**A_T(L/g)**	**B_T(j/mol)**	**r^2**
KAO	0.0044	1.713	0.8937	0.027	0.6398	0.9478	0.0366	6128.05	0.9632
MET	0.000433	5.820	0.0294	0.0029	0.9565	0.8833	0.0224	8225.67	0.9423

K_L: Langmuir constant; Q_m: maximum monolayer capacity; K_F: Freundlich constant; A_T and B_T: Temkin constants

Conclusion

Adsorption of phenol from aqueous solutions onto KAO and MET materials was carried out by batch mode. Results show that the adsorption capacity of phenol on KAO and MET is affected by pH, initial concentration, contact time, sorbent dose; that quantity adsorbed increased with initial concentration of phenol for an equilibrium time of 40 minutes at pH=2. Adsorption kinetics of phenol (chemisorption) is better described by pseudo second-order, and equilibrium is governed by Freundlich and Temkin isotherm models. The adsorption capacity of samples studied is lower than those of commercial activated carbons. These low values are due to the fact that adsorption of low solubility compounds (phenol and other benzene derivatives) are more feasible with hydrophobic materials (activated carbon, porous polymers) and very insignificant with polar hydrophilic adsorbents (silica gel, alumina). Since adsorption is also influenced by interactions between the adsorbate and the surface functional groups of the adsorbent material, basic treatment or molecular grafting (of amines or thiols onto clay) can help increase the adsorption capacity of the clay samples studied. We infer here that adsorbents employed in this study are comparatively more efficient in the elimination of phenol (toxic organic molecule) from aqueous solutions than others cited in the literature.

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