Removal of Phenol from Water by Adsorption onto Sewage Sludge Based Adsorbent

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The aim of this study is to evaluate the adsorption performances of sewage sludge based adsorbent SSBA for the removal of phenol from water. The SSBA was prepared by chemical activation with H_2SO_4 in a mass ratio of 1:1, followed by a pyrolysis at 650°C for 1 h under inert atmosphere. Phenol removal by SSBA was investigated using kinetic and equilibrium experiments. The results demonstrate that phenol sorption to the SSBA reached equilibrium at 2 h with the maximum sorption capacity of 26.16 mg.g^{-1} under given experimental conditions (initial Phenol concentration range = 40–200 mg.l^{-1}; adsorbent dose = 5.0 g.l^{-1} and temperature = 20°C). The phenol removal was high and relatively constant at (pH<pKa), whereas the phenol removal decreased sharply as the solution pH approached a highly alkaline condition (pH>pKa).The results indicate that the pseudo second order model was suitable for describing the kinetic data. Regarding the equilibrium data, the Freundlich isotherm was fitted well. This study demonstrates that SSBA could be used for phenol removal from water.

1. Introduction

Phenol is a toxic weak acid causes an unpleasant taste and odour even at low concentrations in water (Podkościelny and László, 2007). The major sources of phenol pollution in the aquatic environment are wastewaters from paint, pesticide, coal conversion, polymeric resin, petroleum and petrochemicals industries. Introducing phenolic compounds into the environment or degradation of these substances means the appearance of phenol and its derivatives in the environment. The chlorination of natural waters for disinfection produces chlorinated phenols. Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations (Ahmaruzzaman, 2008). Treatment of wastewater containing phenol is a very important need for environmental protection and has been studied by various techniques such as chemical oxidation, biodegradation, membrane filtration, electro coagulation, solvent extraction, photo degradation and adsorption. Among these techniques adsorption is still the most popular and widely used technique for phenol removal. This work focuses on the removal of phenol from water using a low cost adsorbent prepared from sewage sludge by chemical activation with sulphuric acid.

2. Materials and methods

2.1. Raw sewage sludge
Fresh sewage sludge was collected from an urban Wastewater treatment plant (WWTP) of Constantine town, in the Northeast of Algeria. The influent treated is mainly domestic and the plant use biological treatment process with activated sludge. The sludge used in this study was dewatered surplus sludge collected from a sun drying bed, traditionally used as a farmland fertilizer.

2.2 Preparation of the sewage sludge based adsorbent (SSBA)
Collected sample was air dried at 105°C until constant weight. The resulting solid was ground and sieved through 1 mm mesh. Dried sludge was impregnated in (3M) H_2SO_4 solution with the mass ratio of 1:1. The

mixture was magnetically stirred in a beaker for 48 h at ambient temperature. Then, the excess solution was decanted off and the precursor was air dried at 105°C for another 48h.

After that, 15 g of chemical activated sample was placed into a covered ceramic crucible and placed in another big crucible. The cavity between the two crucibles was filled up with fuel coke particles <1 mm, to prevent O_2 from entering the ceramic crucible during pyrolysis operation (Gascó et al., 2005). Then, the sample was pyrolyzed in a muffle furnace. The furnace temperature was gradually increased to 650°C at a rate of 10°C/min, and the final temperature of 650°C maintained for 1 h.

After being pyrolyzed, the sample was washed with 3.0 M HCl to remove the acid-soluble inorganic impurities. Then, the sample was thoroughly washed with hot distilled water until constant pH was reached. After that, the sample was dried at 105°C for 24 h to constant weight. The resulting solid was grounded and sieved to a particle size of 0.125 mm. Finally the powder was stored in desiccators for further use.

2.3 Adsorbate

Phenol (C_6H_5OH) of analytical grade (supplied by Panreac, Spain), was used for the preparation of the stock solution (1.0 g.l^{-1}). The experimental solutions of various initial concentrations (C_0) were prepared by diluting stock solution to the desired concentrations.

2.4 Characterization of SSBA

The BET surface area of porous SSBA was estimated from adsorption-desorption of N_2 at 77.4 K using a Quantachrome NOVA-e2200 analyzer. The pH_{PZC} (point of zero charge) of SSBA was determined according to the procedure described by (Lopez-Ramon et al., 1999).

2.5 Adsorption tests

Batch Adsorption tests of phenol were carried out in brown dark bottles (to reduce photo-oxidation of phenol). The total volume of the reaction solution was kept at 20ml. The stoppred bottles were magnetically shaken at 300 rpm until equilibrium was reached in a thermostat water bath shaker. Blank sorption experiments were performed in the absence of adsorbent, and no sorption of phenol by the walls of the bottles occurred. The effect of solution pH on the removal of phenol was investigated over the pH range from 2–13. The initial solution pH was adjusted using 0.1 and 1.0 N HCl or 0.1 and 1.0 N NaOH. Adsorption equilibrium experiments were performed by stirring 20 ml of phenol aqueous solution with initial concentration of 40–200 mg.l^{-1} in each bottle containing 100 mg of SSBA. The solutions were agitated at different temperatures 20, 30 and 55 °C, respectively. Adsorption kinetic experiments were basically identical to those of equilibrium tests. The aqueous samples were taken out at some intervals. After adsorption, the adsorbent samples were separated by centrifugation at 4000 rpm during 15 min and the supernatants liquids were analyzed for residual phenol concentration using a double-beam spectrophotometer, Shimadzu, model UV-160, at wavelength of 270 nm. The amount of phenol adsorbed onto per gram of adsorbent (qe) and the percentage removal efficiency (R %) were calculated using Eqs. (1) and (2), respectively.

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{1}$$

$$R\% = \frac{C_0 - C_e}{C_0} \cdot 100 \tag{2}$$

Where C_0 and C_e are initial and equilibrium phenol concentrations, respectively (mg.l^{-1}), V is phenol solution volume (l), m is the mass of adsorbent (g).

3. Results and discussion

3.1 Characteristics of SSBA

The resulting SSBA shows an acceptable development of the specific surface area (162.2 m^2/g) compared to the raw sludge which is a non-porous material (< 1 m^2/g). The surface area of the SSBA is relatively small compared to those of the Commercial Activated Carbon (CAC). The pH_{PZC} of SSBA (4.66) indicate that the adsorbent is an acidic material. Therefore, the adsorbent surface is positively charged at pH< 4.66 and negatively charged at pH> 4.66.

3.2 Effect of contact time and initial phenol concentration

The effect of contact time on the rate of phenol removal was investigated at different initial concentrations (50, 100 and 200 mg.l^{-1}) as shown in Figure 1(a).The results indicate that the contact time to reach equilibrium is approximately 120 min for all experiments. Therefore, the chosen contact time of 180 min, used in our experiments, is sufficient to reach equilibrium. It was observed that the adsorption process is extremely fast. In fact, for all experiments more than 77% of the equilibrium adsorption capacity was reached within the first minute. The initial fast adsorption is probably due to the special one-atom-thick layered structure of SSBA, which makes phenol contact immediately with the active sites on the surface of SSBA. With further increasing time, the diminishing availability of the remaining active sites and the decrease in the driving force make it take long time to reach equilibrium. Figure 1(a) also showed that the equilibrium adsorption capacity increased from 9 to 23 mg.g^{-1} with the increasing initial phenol concentration from 50 to 200 mg.l^{-1}. When the initial concentrations increased, the mass transfer driving force became larger and the interaction between phenol and adsorbent was enhanced, hence resulting in higher adsorption capacity.
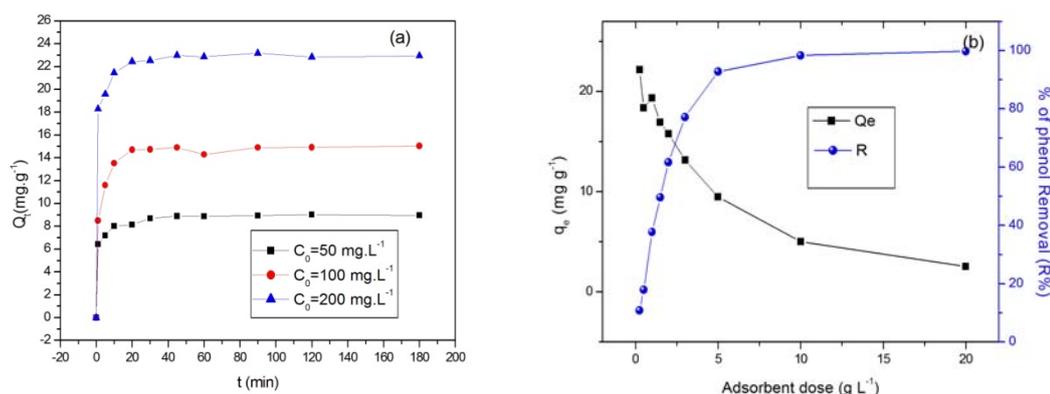

Figure 1: (a) Effect of contact time on the adsorption of phenol (adsorbent dose = 5 g.l^{-1}; initial pH 7.0; T= 20°C) (b) Determination of the optimal dose of SSBA (C_0 = 50 mg.l^{-1}; initial pH 7.0; T= 20°C; t = 3h)

3.3 Effect of adsorbent dose
The effect of adsorbent dose on the adsorption capacity (qe) and the removal percentage (R%) of phenol was studied and is shown in Figure 1(b). As the SSBA dose was increased from 0.25 to 20 g.l−1, the percentage of adsorbed phenol increased from 10.84 % to 99.76%, whereas the adsorption capacity decreases from 22.18 to 2.55 mg g^{-1}. Above 5.0 g.l^{-1} of adsorbent dose, there was no significant increase in the removal rate of phenol, but the adsorption capacity decreased rapidly. Considering q_e and R%, adsorbent dose of 5.0 g.l^{-1} was found to be the optimum SSBA dose and was used for all other experiments.

3.4 Effect of pH
Solution pH is one of the most important parameters to determine the adsorption property of an adsorbent due to its effect on the surface charge of the adsorbent and on the degree of ionization of adsorbate. Phenol as a weak acid with pKa = 10 and it dissociates at pH > pKa, the percentage of the molecular form of phenol can be calculated from the Eq(3).

$$P_m(\%) = \frac{100}{1 + 10^{(pH - pKa)}}$$

(3)

Pm(%) is the percentage of molecular phenol in the solution. From Eq(3) it can be seen that phenol is mainly in molecular form at pH<pKa and in ionic form (phenolate anions) at pH>pKa. In this study the effect of solution pH on the removal of phenol was investigated over the initial pH range from 2–13. The effect of phenol speciation on the adsorption is better explained by calculating the Pm(%) using Eq(3) at different final pH (pH at equilibrium) values and a plot of the Pm(%) and percent of phenol removal (%R) versus final pH are shown in Figure 2(a) which clearly shows that phenol removal is pH independent at pH<pKa (phenol is mainly in molecular form) and highly influenced when pH>pKa (phenol is mainly in ionic form). In fact when phenol is mainly in molecular form, R% value is higher and constant (R ≈ 80 %) and as the pH is increased (pH>pKa), the phenol ionic form increases which implicate a rapid decrease in R%

until it reaches its smallest value of 21% when Pm(%) was practically negligible 1 % at final pH 12. The decrease of R% value when pH>pKa is due to the presence of electrostatic repulsion between the negatively charged adsorbent surface (pH >pH$_{PZC}$) and phenol ionic form. Even though the electrostatic repulsion at final pH 12, a significant removal of 21 % takes place indicating that chemisorption might be involved in the process, similar results were reported by (Bousba and Meniai, 2013) in the case of 2-chlorophenol removal by SSBA.
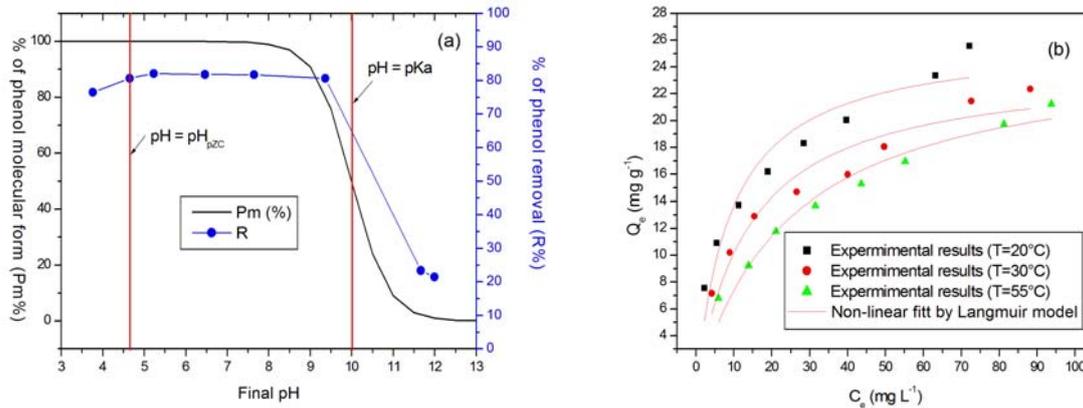

Figure 2: (a) Effect of pH on the removal of phenol (C$_0$ = 100 mg.l^{-1}; T= 20°C; t = 3 h) (b) Langmuir isotherm representation for the adsorption of phenol onto SSBA (T= 20, 30 and 55°C; t = 3 h; C$_0$ = 40-200 mg.l^{-1})

3.5 Isotherm analysis

Several models have been published in the literature to describe the equilibrium adsorption systems. In this paper adsorption isotherms were fitted by the two classical models of Langmuir and Freundlich. Langmuir:

$$q_e = q_m \frac{b.C_e}{1+b.C_e} \tag{4}$$

where q$_m$ (mg.g^{-1}) is the theoretical maximum monolayer adsorption capacity at the constant temperature, and b (l.mg^{-1}) is the Langmuir constant related to the energy of adsorption.

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor R$_L$, which is expressed as:

$$R_L = \frac{1}{1+b.C_0} \tag{5}$$

where b is Langmuir constant (l.mg^{-1}) and C$_0$ is maximum initial phenol concentration (mg.l^{-1}). The value of R$_L$ indicates the shape of Langmuir isotherm to be either unfavorable (R$_L$ >1), linear (R$_L$ =1), irreversible (R$_L$=0), or favorable (0<R$_L$<1). Also the smaller R$_L$ value indicates a highly favourable adsorption. Freundlich:

$$q_e = k_F C_e^{1/n} \tag{6}$$

where k$_F$ (mg.g^{-1}(l.mg^{-1})$^{1/n}$) and n are Freundlich constants related to the multilayer adsorption capacity and the surface heterogeneity, respectively. According to (Hamdaoui and Naffrechoux, 2007) It is generally stated that values of n in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics. The plot of q$_e$ versus C$_e$ for the adsorption of phenol onto SSBA at 20, 30 and 55 °C according to the non-linear form of Langmuir and Freundlich isotherm models were shown in Figures 2(b) and (3a), respectively. The parameters calculated by non-linear regression analysis of Langmuir and Freundlich isotherms were given in Table 2. The adsorption capacity of SSBA decrease with increase in temperature, indicating that the adsorption process is exothermic in nature. It can be seen from Table 2, that the correlation factor R^2 is close to the unity for both models, but with a better fit of the experimental data by means of Freundlich isotherm, which prove the multilayer adsorption and the heterogenity of the SSBA surface. From table 2 it can be seen that the values of Freundlich constant n were found to be within the range of 2–10 witch indicate that the SSBA is good adsorbent for phenol.
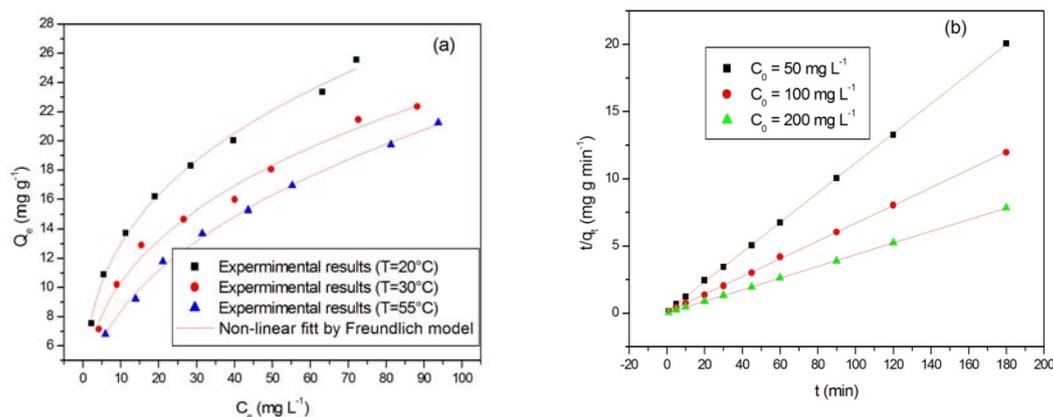
Figure 3: (a) Freundlich isotherm representation for the adsorption of phenol onto SSBA (T= 20, 30 and 55°C; t = 3 h; C_0 = 40-200 mg.l^{-1}) (b) Plot of the pseudo second-order kinetic for the adsorption of phenol onto SSBA (T= 20°C; t= 3 h)

Table 2: Langmuir and Freundlich isotherm parameters for phenol adsorption at 20,30 and 55 °C

T (°C)	Langmuir isotherm				Freundlich isotherm		
	Q_m (mg.g^{-1})	b (l.mg^{-1})	R^2	R_L	k_F (mg.g^{-1}(l.mg^{-1})$^{1/n}$)	n	R^2
20	26.16 ± 1.77	0.109 ±0.028	0.927	0.04-0.19	6.059 ± 0.229	3.02± 0.09	0.996
30	24.15 ± 1.60	0.073±0.017	0.936	0.06-0.26	4.581 ± 0.319	2.82± 0.14	0.989
55	25.39 ± 1.64	0.041±0.007	0.964	0.11-0.38	3.239 ± 0.120	2.42± 0.05	0.998

The comparison of maximum monolayer adsorption of phenol onto various adsorbents was listed in Table 3, which showed that sewage sludge based adsorbent SSBA used in present work had a relatively quite adsorption capacity of 26.16 mg.g^{-1} compared to some data of low cost adsorbents obtained from the published literature.

Table 3: Comparison of the maximum monolayer adsorption of phenol onto various adsorbents

Q_m (mg.g^{-1})	Adsorbent	References
59.2	Red mud	(Gupta et al., 2004)
17.1	Coal fly ash	(Sarkar and Acharya, 2006)
13.3	Samla coal	(Ahmaruzzaman and Sharma, 2005)
23.83	Bagasse fly ash	(Srivastava et al., 2006)
26.16	SSBA activated with H_2SO_4	Present work

3.6 Adsorption kinetics

The kinetic study is helpful in prediction of adsorption rate constants, equilibrium adsorption capacity and adsorption mechanism. The capability of pseudo-first-order PFO and pseudo-second-order PSO kinetic models were examined in this study at three different initial concentration of phenol (50,100,200 mg.l^{-1}) and at constant temperature of 20°C.

The linear form of pseudo first-order model of Lagergren is generally expressed as follows :

$$ln(q_e - q_t) = ln(q_e) - k_1 t \tag{7}$$

where q_e and q_t are the adsorption capacity of phenol per unit weight of SSBA at equilibrium and at time t (min), respectively (mg.g^{-1}), and k_1 is the PFO rate constant (min^{-1}).

k_1 and qe values were determined from the slope and intercept of the plots of $ln(q_e−q_t)$ versus t (figure not shown) for different concentrations of phenol and are listed in Table 3. From the data in Table 3, it can be seen that at all studied concentrations, the correlation coefficients R^2 are small. Also, the experimental qe values do not agree with the calculated ones, suggesting that the applicability of the PFO model to the adsorption processes of phenol onto SSBA is unfeasible.

The linear form of PSO model is expressed as follows :

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

(8)

where k_2 is the PSO rate constant ($g.mg^{-1}.min^{-1}$). The values of q_e and k_2 were determined from the slope and intercept of the plot of t/q_t versus t. The plot of t/q_t versus t at different concentrations is shown in Figure 3(b). The data obtained for the PSO kinetic model at different concentrations is presented in Table 4. In this case, the fitting of the expermiental data in the pseudo-second-order equation showed excellent linearity with high correlation coefficient ($R^2 > 0.999$). On the other hand, the calculated values of qe obtained from the pseudo second order model agreed perfectly with the experimental values of qe at three initial concentrations, respectively. An analysis of the data in Table 4 suggests that the kinetics of adsorption of phenol onto SSBA can be explained accurately by the PSO kinetic model.

Table 4: *The PFO and PSO kinetic parameters for the adsorption of phenol onto SSBA*

C_0 (mg.l^{-1})	q_e exp (mg.g^{-1})	pseudo first-order model **PFO**			pseudo second-order model **PSO**			
		k_1 (min^{-1})	q_e cal (mg.g^{-1})	R^2	k_2 (g.mg^{-1}min^{-1})	$k_2 q_e$ (min^{-1})	q_e cal (mg.g^{-1})	R^2
50	9	0.13	8.90	0.8805	0.0978	0.88	9.05	0.9999
100	15	0.07	10.19	0.5971	0.0560	0.85	15.09	0.9998
200	23	0.16	64.00	0.8430	0.0920	2.11	23.02	0.9999

4. Conclusions

The adsorption of phenol from water using SSBA activated with H_2SO_4 was investigated. Various experimental parameters such as contact time, adsorbent dose, initial phenol concentration, temperature and solution pH were optimized. The adsorption was found to be highly influenced by initial phenol concentration and phenol speciation which is directly related to solution pH. Equilibrium study show that the data fit very well in the Freundlich equation of multilayer adsorption but showed small deviation with the Langmuir equation, this result indicate the heterogeneity of the adsorbent surface. The values of R^2 obtained from pseudo second-order model were higher than 0.999, indicating that the adsorption process obeyed the pseudo second-order model. Finally the adsorption experiments indicated that sewage sludge based adsorbent SSBA was efficient adsorbent for the removal of phenol from water.

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