Adsorption of 2-Chlorophenol onto Sewage Sludge based Adsorbent: Equilibrium and Kinetic Study

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The adsorption capacity of sewage sludge based adsorbent (SSBA) for the removal of 2-chlorophenol (2-CP) from aqueous solutions, was considered in the present study. 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. The produced adsorbent was characterized in terms of the specific surface area, the pH at zero charge point (pH_{PZC}) and the surface functional groups. Batch adsorption experiments were carried out under different conditions including the adsorbent dose, the contact time, the initial 2-CP concentration, the solution pH and the ionic strength, in order to investigate their effects on the retention capacity of the solid support. The Langmuir and Freundlich isotherm models were tested to examine the adsorption behavior. The equilibrium data were well fitted by the Freundlich model. The maximum monolayer adsorption capacity of SSBA was found to be 47.98 mg.g^{-1} at 20 °C. Finally the kinetic studies indicated that adsorption process followed the pseudo second-order model. In conclusion SSBA showed quite good capabilities in removing 2-CP from aqueous solutions.

1. Introduction

Sewage sludges are the main waste products in wastewater treatment plants. The annual production exceeds 10 and 7 Mt/y in the European Union and in the USA, respectively (Cyr et al., 2007). Therefore, the handling and disposal of this waste is an issue of particular concern. Traditional methods for the recycling and reuse of sewage sludge are spreading on agricultural land, incineration and land filling. However the use of these three traditional methods has been limited by the implementation of a new legislation in recent years (Fytili and Zabaniotou, 2007).

The decline of the traditional disposal solutions for sewage sludge has increased the need for effective but much more costly alternatives. However since sewage sludge is carbonaceous in nature, its conversion into adsorbents might be a promising alternative to its valorisation (De Filippis et al., 2013).

This work focuses on the preparation and characterization of a low cost adsorbent from sewage sludge by chemical activation using sulphuric acid. The resulting adsorbent is tested for 2-chlorophenol removal from water. In fact chlorophenols are present in wastewaters issuing from many industrial processes and they must be removed due to their high toxicity.

2. Materials and methods

2.1 Raw sewage sludge
Fresh sewage sludge was collected from an urban Wastewater treatment plant of Constantine, a city in the Northeast of Algeria. The mainly treated influent is domestic and the plant uses 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)

A collected sample was air dried at 105 °C, and then impregnated in 3.0 M H_2SO_4 solution with a mass ratio of 1:1 for 48 h with a magnetic agitation. Then, the excess solution was decanted off and the settled solid was air dried at 105°C for further 48 h. After that, 15 g of chemical activated sample was pyrolysed in a muffle furnace with a gradual temperature increase up to 650 °C at a rate of 10 °C/min, and maintained constant for 1 h.

After being pyrolysed, the sample was washed with 3.0 M HCl and hot distilled water, up to a constant pH, followed by a drying at 105 °C for 24 h to constant weight. Finally the resulting adsorbent was ground and sieved to a particle size of 0.125 mm.

2.3 Adsorbate

2-Chlorophenol (C_6H_5ClO) of analytical grade (supplied by Fluka, Germany), was used for the preparation of the stock solution (1.0 g L^{-1}). Experimental solutions of various initial concentrations (C_0) were prepared by diluting stock solution to the desired concentrations.

2.4 Characterization of sewage sludge and SSBA

The proximate analysis was conducted according to ASTM D3172-89 standards and the result was expressed in terms of moisture, ash, volatile matter and fixed carbon contents. The BET surface area of the raw material and porous SSBA were 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). Base-acid titration based on Boehm's method (Boehm, 1994) was performed to measure the total amount of basic and acidic groups on the adsorbent surface, using solutions of NaOH (0.1 N) and HCl (0.1 N).

2.5 Adsorption tests

Batch Adsorption tests of 2-CP were carried out at 20 °C in brown dark bottles (to reduce photo-oxidation of 2-CP) and the total volume of the reaction solution was kept at 20 mL. The sealed bottles were magnetically shaken at 300 rpm until equilibrium was reached in a thermostat water bath shaker. The effect of solution pH on the removal of 2-CP was investigated over the pH range from 3–12. The initial solution pH was adjusted using 0.1 N HCl or 0.1 N NaOH. The effect of salt ionic strength on the adsorbed amount of 2-CP was discussed over the NaCl or $CaCl_2$. Adsorption equilibrium experiments were performed by stirring 20 mL of 2-CP aqueous solution with initial concentration of 20–200 mg L^{-1} in each bottle containing 40 mg of SSBA. Adsorption kinetic experiments were basically identical to those of equilibrium tests. The aqueous samples were taken out at fixed intervals. After adsorption, the adsorbent samples were separated by centrifugation at 4,000 rpm during 15 min and the supernatants liquids were analyzed for residual 2-CP concentration using a double-beam spectrophotometer, Shimadzu, model UV-160, at wavelengths of 274 and 293 nm, with respect to the molecular and ionic forms of 2-CP (Chuang et al., 2008). The adsorbed amount of 2-CP onto a gram of adsorbent (q_e) and the percentage removal efficiency (R %) were calculated using Eq(1) and Eq(2).

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

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

Where C_0 and C_e are initial and equilibrium 2-CP concentrations, respectively (mg L^{-1}), V is 2-CP solution volume (L), m is the mass of adsorbent (g)

3. Results and discussion

3.1 Characteristics of raw sewage sludge and SSBA

The main physicochemical characteristics of the raw sludge and SSBA are summarized in table 1 from which it is clearly seen that 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). But the surface area of he SSBA is relatively small compared to those of the Commercial Activated Carbon (CAC). This can be explained by the presence of a large amount of ash in the raw sludge, whereby the ashes are the nonporous inorganic portion of the sludge. On the other hand, Table 1 shows that the surface of the SSBA contains a high concentration of acidic groups. This is due to activation by a highly concentrated sulphuric acid. Moreover, the pH_{PZC} of SSBA (4.66) indicated that the adsorbent is an acidic material. Therefore, the adsorbent surface is positively and negatively charged at pH lower and greater than 4.66.

Table 1: Characteristics of raw sewage sludge and SSBA

Parameters	Raw sewage sludge	SSBA
Moisture %	2.32	2.09
Ash % (dry basis)	43.95	61.84
Volatile matter % (dry basis)	53.24	27.90
Fixed carbon % (dry basis)	2.81	10.25
BET surface area (m^2/g)	0.96	166.20
Surface pH	8.14	5.54
pH_{PZC}	not determined	4.66
Total acidic groups (mmol/g)	not determined	2.857
Total basic groups (mmol/g)	not determined	0.204

3.2 Effect of contact time and initial 2-CP concentration

The effect of contact time on the rate of the removal of 2-CP was investigated at different initial 2-CP concentrations (50, 100 and 200 mg L^{-1}) as shown in Figure 1(a). The results indicate that the contact time to reach the adsorption equilibrium is approximately 2h for all experiments. Therefore, the chosen contact time of 6 h, used in our experiments, is more than sufficient to reach equilibrium. It was observed that the adsorption process is very fast. In fact, for the three concentrations more than 70 % of total 2-CP adsorption capacity was reached within the first 5 min. Figure 1(a) also showed that the equilibrium adsorption capacity increased from 23.65 to 51.73 mg g^{-1} with the increasing initial 2-CP concentration from 50 to 200 mg L^{-1}.
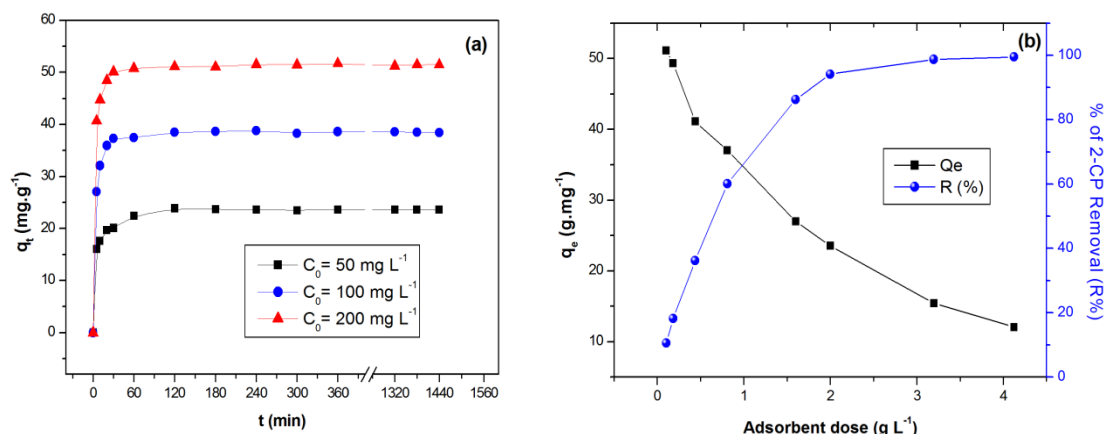

Figure 1: (a) Effect of contact time on the adsorption of 2-CP (adsorbent dose = 2 g L^{-1}; initial pH 7.0; T = 20 °C) (b) Determination of the optimal dose of SSBA (C_0 = 50 mg L^{-1}; initial pH 7.0; T = 20 °C; t = 6 h)

3.3 Effect of adsorbent dose

The effect of adsorbent dose on the adsorption capacity (qe) and the removal percentage (R %) of 2-CP was studied and is shown in Figure 1(b). As the SSBA dose was increased from 0.1 to 4 g L^{-1}, the percentage of adsorbed 2-CP increased from 10% to 99.51 %. However, the adsorption capacity (q_e) presented the opposite trend. Above 2.0 g L^{-1} of adsorbent dose, there was no significant increase in the removal rate of 2-CP, but the q_e decreased rapidly. Considering q_e and R%, adsorbent dose of 2.0 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. 2-CP as a weak acid with pKa = 8.56 and it dissociates at pH > pKa, the percentage of the molecular form of 2-CP can be calculated from the Eq(3).

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

(3)

CP_m(%) is the percentage of molecular 2-CP in the solution. From Eq(3) it can be seen that 2-CP is mainly in molecular form at pH<pKa and in ionic form (chlorophenolate anions) at pH>pKa. In this study the effect

of solution pH on the removal of 2-CP was investigated over the initial pH range from 3–11. The effect of 2-CP speciation on the adsorption is better explained by calculating the $CP_m(\%)$ using Eq(3) at different final pH (pH at equilibrium) values and a plot of the $CP_m(\%)$ and percent of 2-CP removal (%R) versus final pH are shown in Figure 2(a) which clearly shows that 2-CP removal is pH independent at pH<pKa (2-CP is mainly in molecular form) and highly influenced when pH>pKa (2-CP is mainly in ionic form). In fact when 2-CP is mainly in molecular form, R% value is higher and constant (R ≈ 78 %) and as the pH is increased (pH>pKa), the 2-CP ionic form increases which implicate a rapid decrease in R% until it reaches its smallest value of 24 % when $CP_m(\%)$ was practically negligible 0.06 % at final pH 11.78. 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 2-CP ionic form. Even though the electrostatic repulsion at final pH 11.78, a significant removal of 24 % takes place indicating that chemisorption might be involved in the process, similar results were reported by (Namasivayam and Kavitha, 2003).

3.5 Effect of salt ionic strength

The influence of salt ionic strength on the adsorption capacity is important, since large amounts of salts are commonly present in wastewater. The influence of changing salt ionic strength on the adsorption process was discussed over the NaCl or $CaCl_2$ concentration range from 0.01 to 1 mol L^{-1}.The results are shown in Figure 2(b), where no significant influence of ionic strength was observed.
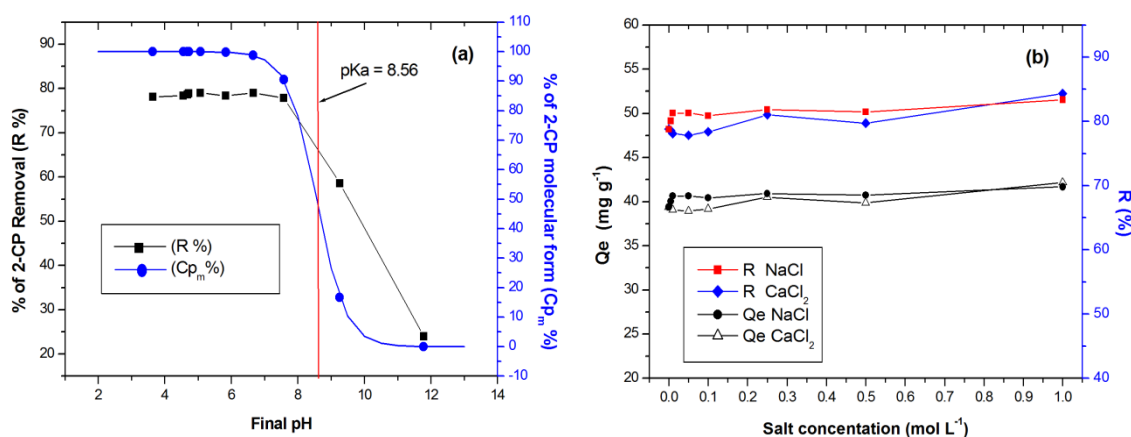

Figure 2: (a) Effect of pH on the removal of 2-CP (C_0 = 100 mg L^{-1}; T = 20 °C; t = 6 h) (b) Effect of salt ionic strength on the adsorption of 2-CP (C_0 = 100 mg L^{-1}; T= 20 °C; t= 6 h)

3.6 Isotherm analysis

Several models have been reported in the literature to describe the equilibrium adsorption systems. However in this present study, the two classical models of Langmuir and Freundlich were tested. The former is expressed as follows:

$$q_e = q_m \frac{b.C_e}{1+b.C_e}$$ (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:

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

where b is Langmuir constant (L mg^{-1}) and C_0 is maximum initial 2-CP 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 a smaller R_L value indicates a highly favourable adsorption.

The Freundlich model is expressed as follows:

$$q_e = k_F C_e^{1/n}$$ (6)

where k_F (mg g^{-1}(L mg^{-1})$^{1/n}$) and 1/n are Freundlich constants related to the multilayer adsorption capacity and the surface heterogeneity, respectively. When (1/n >1) the adsorption is unfavorable, (1/n=1) the adsorption is homogeneous and (0 <1/n<1) the adsorption is favorable.

The plot of q_e versus C_e for the adsorption of 2-CP onto SSBA at 20 °C according to the non-linear form of Langmuir and Freundlich isotherm models were shown in Figure 3(a) and their parameters were calculated by non-linear regression analysis of the corresponding isotherms and are given in Table 2.
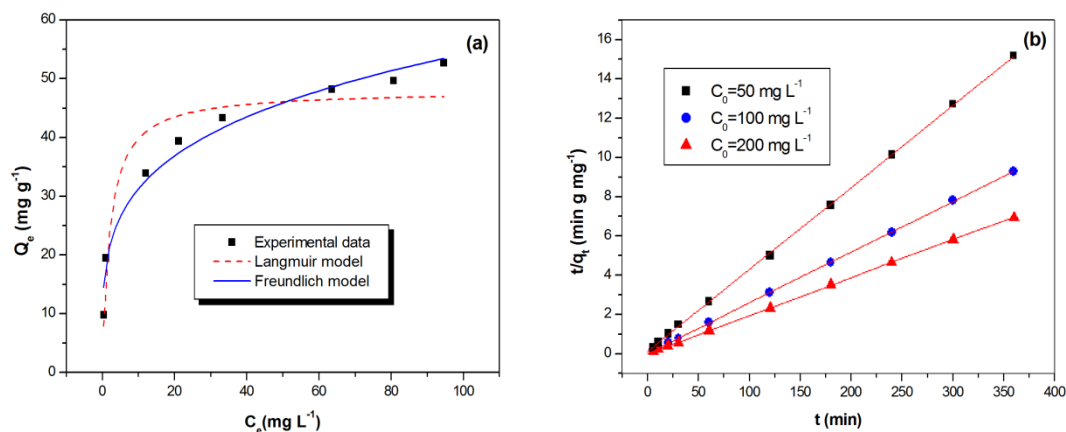

Figure 3: (a) Langmuir and Freundlich isotherms representation for the adsorption of 2-CP onto SSBA (T= 20 °C; t= 6 h; C_0 = 20-200 mg L^{-1}) (b) Plot of the pseudo second-order kinetic for the adsorption of 2-CP onto SSBA (T= 20 °C; t= 6 h)

It can be seen 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, indicating the multilayer adsorption and the heterogenity of the SSBA surface. From Table 2 it can be seen that the values of R_L and 1/n were found to be within the range of 0–1, indicating that the adsorption of 2-CP onto SSBA is favoroble according to both Langmuir and Freundlich models.

Table 2: Langmuir and Freundlich isotherm parameters for 2-CP adsorption onto SSBA at 20 °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})$^{1/n}$)	1/n	R^2
47.977 ± 2.438	0.485 ±0.186	0.918	0.0102	18.001 ± 1.428	0.239± 0.020	0.977

3.7 Adsorption kinetics

A kinetic study was carried out for the prediction of adsorption rate constants, equilibrium adsorption capacity and adsorption mechanism. The capability of pseudo-first and second order kinetic models were examined in this study at three different initial concentation of 2-CP (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 :

$$ln(q_e - q_t) = ln(q_e) - k_1 t \qquad (7)$$

where q_e and q_t are the adsorption capacity of 2-CP per unit weight of SSBA at equilibrium and at time t (min), respectively (mg g^{-1}), and k_1 is the pseudo first-order 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 2-CP 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 q_e values do not agree with the calculated ones, suggesting the non applicability of the pseudo-first-order model to the adsorption processes of 2-CP onto SSBA.

The linear form of pseudo second-order model is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where k_2 is the pseudo second-order 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, as shown in Figure 3(b). The data obtained for the pseudo-second order kinetic model at different concentrations is presented in Table 3. In this case, the fitting of the experimental data in the pseudo-second-order equation showed excellent linearity with high correlation coefficient ($R^2 > 0.999$). On the other hand, the calculated rersults of qe by means of the pseudo second order model agreed perfectly with the experimental values at three initial concentrations, respectively. An analysis of the data in Table 3 suggests that the kinetics of adsorption of 2-CP onto SSBA can be explained accurately by the pseudo-second-order kinetic model.

Table 3: The pseudo first-order and pseudo second-order kinetic parameters for the adsorption of 2-CP onto SSBA

C_0 (mg g^{-1})	q_e(exp) (mg g^{-1})	Pseudo-first-order model			Pseudo-second-order model		
		k_1 (min^{-1})	q_e(cal) (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e(cal) (mg g^{-1})	R^2
50	23.650	0.030	8.615	0.9873	0.0126	23.900	0.9998
100	38.826	0.027	6.987	0.8546	0.0164	38.790	0.9999
200	51.728	0.023	6.290	0.7645	0.0132	51.813	0.9999

4. Conclusions

In this study, the ability of sewage sludge based adsorbent (SSBA) to remove 2-Chlorophenol (2-CP) from aqueous solution was investigated. From the results of the present work, it can be said that SSBA showed quite good capabilities in removing 2-CP from water.

The adsorption of 2-CP onto SSBA was found to be highly influenced by initial 2-CP concentration and 2-CP speciation which is directly related to solution pH. Equilibrium study showed that 2-CP adsorption data could best be fitted with the Freundlich equation of multilayer adsorption, contrarily to Langmuir monolayer model where slight deviations were obtained, indicating heterogeneity of the adsorbent surface. Finally obtained experimental kinetic results could be represented using pseudo second order model.

References

Boehm H., 1994. Some aspects of the surface chemistry of carbon blacks and other carbons, Carbon, 32, 759-769.

Chuang Y.H., Tzou Y.M., Wang M.K., Liu C.H., Chiang P.N., 2008. Removal of 2-chlorophenol from aqueous solution by Mg/Al layered double hydroxide (LDH) and modified LDH, Ind. Eng. Chem. Res., 47, 3813–3819.

Cyr M., Coutand M., Clastres B., 2007. Technological and environmental behavior of sewage sludge ash (SSA) in cement-based materials, Cement Concrete Res., 37, 1278–1289.

De Filippis P., Di Palma L., Petrucci E., Scarsella M., Verdone N., 2013, Production and Characterization of Adsorbent Materials from Sewage Sludge by Pyrolysis, Chemical Engineering Transactions, 32, 205-210 DOI: 10.3303/CET1332035.

Fytili D., Zabaniotou A., 2007. Utilization of sewage sludge in EU application of old and new methods-a review, Renew. Sustain. Energy Rev., 12, 116-140.

Lopez-Ramon M.V., Stoeckli F., Moreno-Castilla C., Carrasco-Marin F., 1999. On the characterization of acidic and basic surface sites on carbons by various techniques, Carbon, 37, 1215-1221.

Namasivayam C., Kavitha D., 2003. Adsorptive removal of 2-chlorophenol by low-cost coir pith carbon, J. Hazard. Mater., B98, 257–274.