Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.795716

51 (2013) 5014–5020
July

Taylor & Francis
Taylor & Francis Group

Elimination of organic pollutants from wastewater. Application to p-nitrophenol

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Received 31 August 2012; Accepted 10 April 2013

ABSTRACT

The present study concerns the elimination of a phenolic compound such as p-nitrophenol from aqueous solutions, by adsorption onto sawdust. These compounds are recognized as organic pollutants because of their high toxicity and possible accumulation in the environment. The effects of various operating parameters such as the pH of the solution, the contact time, the initial concentration and the adsorbent dose, on the adsorption of p-nitrophenol, were investigated. The experimentally determined adsorption equilibrium data for p-nitrophenol was best fitted by the Freundlich isotherm model. The p-nitrophenol adsorption rate followed a pseudo-second-order kinetics. A competitive adsorption involving p-nitrophenol, o-chlorophenol and phenol was also considered and the maximum adsorption capacity varied in an increasing order as p-nitrophenol > o-chlorophenol > phenol. Finally this study showed that sawdust can be regarded as an interesting adsorbent for the elimination of organic pollutants such as aromatic compounds which are usually encountered in many industrial wastewater effluents.

Keywords: Sawdust; Phenols; p-nitrophenol; Adsorption; Retention; Freundlich

1. Introduction

Generally, industrial, agricultural, and domestic human activities may result in drastic environmental problems. One can cite global warming, soil and ground waters pollutions, etc. due to certain inorganic or organic compounds [1]. The latter's are the main interest of the present.

One of the most important classes of organic contaminants is Phenol and its derivatives [2]. They are known to be carcinogens and have important ecological consequences on soil and waters. They are also present in effluents issuing from various industries such as coal conversion, pharmaceutical, petroleum refining, petrochemicals, steel, paper, textile, food, pesticides industries, etc. [3].

Nitrophenols are common by-products of many industrial processes and among the most frequent

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Presented at the Conference on Membranes in Drinking and Industrial Water Production.
Leeuwarden, The Netherlands, 10–12 September 2012.
Organized by the European Desalination Society and Wetsus Centre for Sustainable Water Technology

organic pollutants in agricultural wastewaters. They may be formed in air as a result of the atmospheric photochemical reactions of several aromatic compounds formed from anthropogenic sources [4]. They are classified as compounds exhibiting moderate to high toxicity in the aquatic environment and are also characterized as one of the most challenging classes of contaminants requiring removal from wastewater streams [5].

p-nitrophenol, also known as 4-nitrophenol, is one of such important organic compounds. It is a fine intermediate chemical, serving as a precursor of pharmaceuticals and pesticides [6]. p-Nitrophenol is known to be persistent, bioaccumulative and highly toxic. It can penetrate the human body through all routes and its toxic action is similar to that of aniline, contributing to the conversion of hemoglobin to methamoglobin, due to the oxidation of iron (II) to iron (III), hence resulting in an oxygen deficit in the body [7]. Therefore, the complete removal of p-nitrophenol or in some cases reduction of its concentration in wastewaters to an acceptable level has become a major challenge.

They are many methods for removing p-nitrophenol from aqueous solutions and one can cite liquid extraction [8], advanced oxidation processes [9], biological degradation, UV-oxidation [2] and adsorption which is the main concern of the present study. The choice of this technique was mainly guided by the fact that it is an easy and simple operation, and relatively less costly particularly if a free, abundant and performing adsorbent like sawdust is used.

2. Experimental

2.1. Adsorbate and solution

Analytical-reagent grade p-nitrophenol supplied by *PRS Chiminova* was used as the adsorbate in adsorption. A stock solution was prepared by dissolving the required amount of p-nitrophenol in distilled water without pH adjustment. Working solutions of the desired concentrations were obtained by successive dilutions.

2.2. Preparation of carbonized sawdust

Sawdust obtained from locally used wood was used. It was washed with hot distilled water to remove impurities like dust, and then dried at 80°C until a constant weight. The sorbent was activated with 1 N H_2SO_4 used in the ratio 1/10 (sawdust: H_2SO_4, w/w) at 150°C for 24 h, then soaked in 1% sodium bicarbonate solution overnight to remove residual acid. The mixture was dehydrated in an oven overnight at 105°C. The carbonized sorbent was then dried and finally sieved to discrete sizes.

2.3. Batch equilibrium and kinetic studies

In adsorption equilibrium, experiments were conducted in a set of 100 mL Erlenmeyer flasks, where solutions of p-nitrophenol (65 mL) with different initial concentrations (5–100 mg/L) were added in these flasks. Equal masses of 0.65 g of activated sawdust of particle size $\leqslant 0.315$ mm were added to p-nitrophenol solutions and each sample was kept at 20 ± 3°C to reach equilibrium of the solid–solution mixture. The pH of the solutions was adjusted with NaOH 0.1 M (1 M) and HNO_3 0.1 M (1 M).

A similar procedure was followed for another set of Erlenmeyer flask containing the same p-nitrophenol concentration without activated carbon to be used as a blank. The flasks were then removed from the shaker and the final concentration of p-nitrophenol in the solution was analyzed using a spectrophotometer UV–(UV 160 A SHIMADZU). Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by

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

where C_0 and C_e (mg/L) are the liquid-phase concentrations of p-nitrophenol at initial and equilibrium, respectively. V (L) is the volume of the solution, and W (g) is the mass of dry adsorbent used.

The procedures of kinetic experiments were basically identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of p-nitrophenol were similarly measured.

3. Results and discussion

3.1. Effect of pH

The pH of the solution is important for its effect on the adsorbent and sorbate since it influences the respective present functional groups [10]. Therefore, adsorption of p-nitrophenol was studied over pH range of 2.00–10.02 as shown in Fig. 1 where it can be observed that the removal of p-nitrophenol increases with increasing pH from 0.62770 mg/g at pH equal 2.0 to 1.88310 mg/g at pH equal 6.0. This can be explained by solubility and equilibrium dissociation.

An inverse relationship exists between sorbate solubility and its adsorption potential [11] where a low solubility implies that weak forces exist between solvent and sorbate molecule, resulting in high amount of

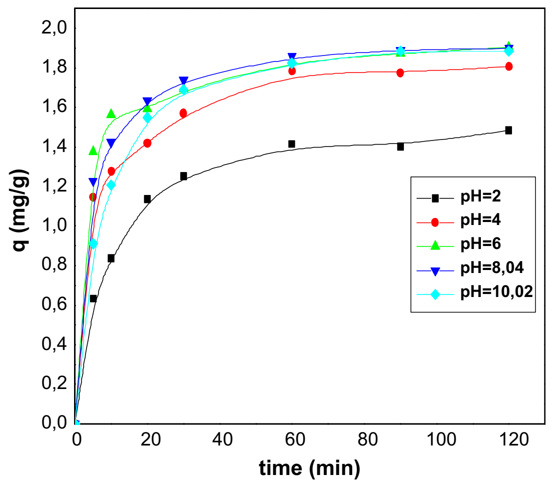


Fig. 1. Effect of pH on the retention of p-nitrophenol $C_0 = 20$ mg/l, $V = 500$ rpm, $t = 180$ min, $T = 20 \pm 3$°C, $d \leqslant 0.315$ mm, $r = 10$ g/l.

uptake. A decrease in the adsorption at higher pH may possibly be due to the increased solubility of p-nitrophenol and the abundance of OH^- ions thereby increasing hindrance to diffusion of phenolate anions. p-Nitrophenol moderate acid with $pK_a = 7.1$ dissociates at $pH > pK_a$ to the anionic form and the sawdust surface is negatively charged [12]. This will generate repulsion between sorbate and adsorbent and the amount of p-nitrophenol adsorbed will be very small as shown in Fig. 1. While at acidic pH, the percentage removal was higher because p-nitrophenol was not dissociated and the dispersion interactions predominated.

3.2. Effect of contact time

Fig. 2 shows the effect of contact time on the removal of p-nitrophenol. The saturation curves rises sharply during the initial stages, indicating that there are a great number of readily accessible vacant sites. Afterwards a plateau is reached in all curves indicating a saturation of the adsorbent, after about 3 h of stirring time. Therefore an equilibrium time of 3 h was assumed for all further experimental runs.

3.3. Effect of initial concentration

The effect of the initial concentration of p-nitophenol on the adsorption was studied in the range of 5–100 mg L^{-1} as shown in Fig. 3. It is found that, the adsorption of p-nitrophenol onto activated sawdust or activated carbon obtained from sawdust was found to be concentration dependent. The removal of p-nitrophenol increases with increase of initial concentration. The removal curves are smooth and continuous, indicating the formation of monolayer coverage of the p-nitrophenol molecules onto the outer surface of the adsorbent. The adsorption capacity at equilibrium (q_e) increased from 0.493965759 to 9.40387314 mg/g with an increase in the initial concentration of p-nitophenol from 5 to 100 mg L^{-1}. At high concentration of p-nitrophenol the ratio of weight of phenol to available surface area was high. Three consecutive mass transport steps are associated with the adsorption of solute from solution by porous adsorbent [13]. First, the adsorbate migrates through the solution, i.e. a film diffusion, followed by solute movement from particle surface into internal site by

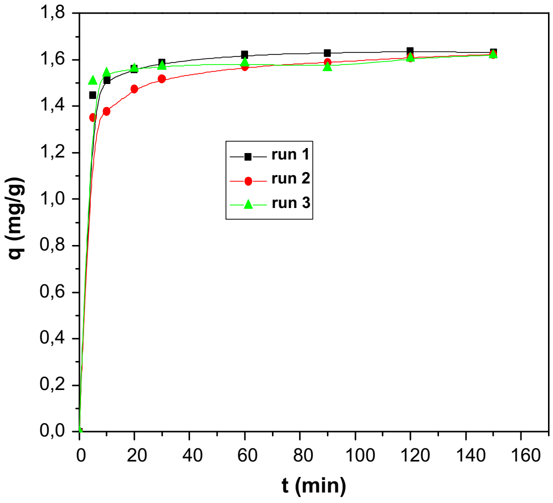


Fig. 2. Effect of contact time on the retention ofp-nitro phenol: $C_0 = 20$ mg/l, $V = 500$ rpm, $T = 20 \pm 3$°C, $d \leqslant 0.315$ mm, $r = 10$ g/l, pH = 5.79.

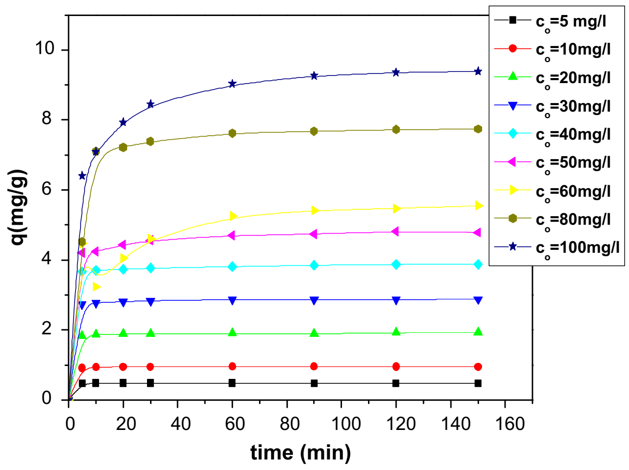


Fig. 3. Effect of initial concentration on the retention of p-nitrophenol: $V = 500$ rpm, $t = 180$ min, $T = 20 \pm 3$°C, $d \leqslant 0.315$ mm, $r = 10$ g/l, pH = 5.79.

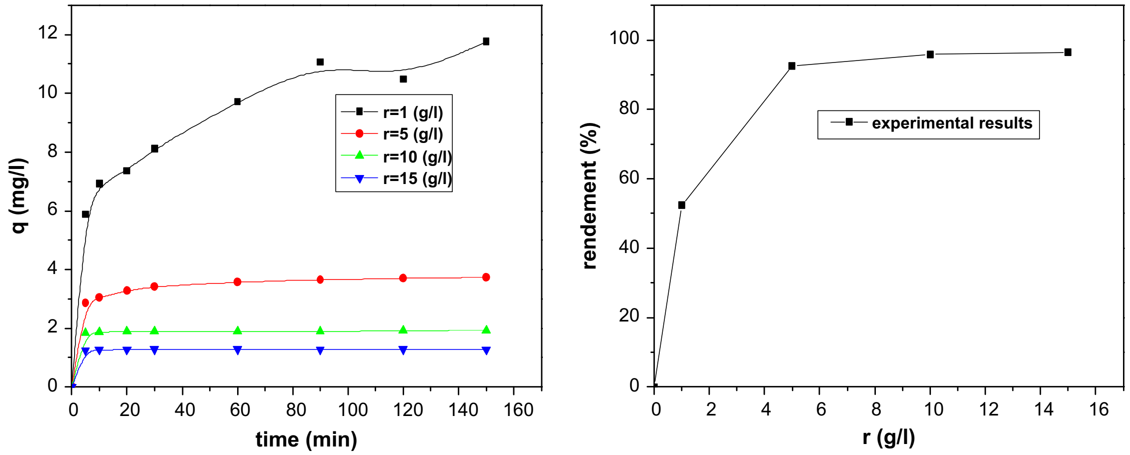


Fig. 4. Effect of adsorbent dose on the retention of p-nitrophenol: $C_0 = 20\,\mathrm{mg/l}$, $V = 500\,\mathrm{rpm}$, $T = 20 \pm 3^\circ\mathrm{C}$, $d \leqslant 0.315\,\mathrm{mm}$, $\mathrm{pH} = 5.79$.

pore diffusion and finally the adsorbate is adsorbed into the active sites at the interior of the adsorbent particle. This phenomenon took relatively long contact time.

3.4. Effect of adsorbent dose

The results obtained from this investigation are shown in Fig. 4. The solid adsorbent mass was varied while the solution volume of adsorbate was kept constant. The data show that increasing sorbent dosage led to an increase in solid–liquid ratio (r g/l) and a decrease of amount uptake and increase of the adsorption percentage of p-nitrophenol. The amount of adsorption decreased from 11.7667696 to 1.26971653 mg/g and the percentage in adsorption increased from 52.399% to 96.451%. As the activated sawdust dose was increased from $r = 1\,\mathrm{g/l}$ to $r = 15\,\mathrm{g/l}$, respectively. In fact, this is attributed to an increase in the available surface area—thus the active sites.

3.5. Adsorption isotherm

Adsorption isotherm is very important to describe how solutes interact with adsorbents, and is critical in the conception of new adsorbents. The Langmuir and Freundlich isotherm models were used to describe the relationship between the amount of p-nitrophenol adsorbed and its equilibrium concentration in solutions. The Langmuir isotherm is valid for monolayer adsorption on a surface containing a finite number of identical sites. The model assumes uniform adsorption on the surface and no transmigration in the plane of the surface [14]. The linear form of the Langmuir isotherm can be represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \tag{2}$$

where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, q_0 and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively.

The Freundlich isotherm is given as [15]:

$$q_e = K_F C^{1/n} \tag{3}$$

where K_F ((mg/g)(L/mg)$^{1/n}$) is roughly an indicator of the adsorption capacity and ($1/n$) of the adsorption intensity. Value of $n > 1$ represents a favorable adsorption condition [16]. The linear form of Eq. (3) is

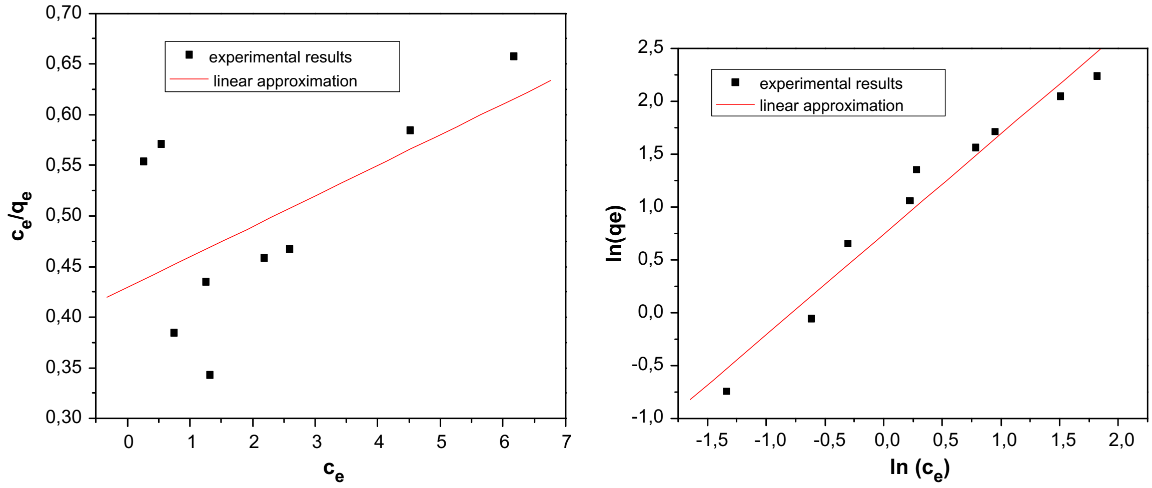
$$\ln q_e = \ln K_F + (1/n) \ln C_e \tag{4}$$

In order to asses these isotherms and their reliability to correlate experimental results, the theoretical plots of each isotherm are shown with the experimental data for the adsorption of p-nitrophenol in Fig. 5.

It is seen from the linearity of plots in Fig. 5 that the adsorption of p-nitrophenol onto activated sawdust follows Freundlich isotherm model with regression constant $R^2 = 0.97794$. The values of Langmuir and Freundlich constant are listed in Table 1.

3.6. Adsorption kinetics

The kinetics of adsorption data was processed to understand the dynamics of adsorption process in terms of the order of rate constant. In order to investigate the mechanism of adsorption, the rate constants



(a) linear Langmuir Adsorption Isotherm

(b) linear Freundlich Adsorption Isotherm

Fig. 5. Adsorption Isotherm for p-nitrohenol with carbonized sawdust at 20 ± 3˚C.

Table 1
Isotherms constants for adsorption of p-nitrophenol onto activated sawdust at 20 ± 3˚C

Models	Constants	R^2
Langmuir	$b = 0.07031523$ (mg/g) $q_0 = 33{,}1{,}345{,}262$ (l/mg)	0.58324
Freundlich	$K_F = 2.1000265$ $(\mathrm{mg/g(l/mg)}^{1/n})$ $n = 1.05386293$	0.97794

of chemical adsorption for p-nitrophenol were determined as pseudo-first-order kinetic model:

$$\frac{dq_t}{dt} = K_1 \times (q_e - q_t) \tag{5}$$

where q_e and q_t refer to the amount of phenol adsorbed (mg/g) at equilibrium and at any time, t (min), respectively, and $k1$ is the equilibrium rate constant of pseudo-first-order sorption (1/min). After definite integration by application of the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (5) becomes

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{6}$$

The sorption rate constant, k_1, can be calculated by plotting ln $(q_e - q_t)$ versus t. In many cases, the first-order equation of Lagergren does not fit well with the whole range of contact time and is generally applicable over the initial stage of the adsorption processes [17].

Kinetic data were further treated with the pseudo-second-order kinetic model [18]. Contrarily to the other model, pseudo second order model predicts the behavior over the whole range of adsorption and is in agreement with an adsorption mechanism being the rate controlling step. The pseudo-second-order equation can be written as

$$\frac{dq_t}{dt} = K_2 \times (q_e - q_t)^2 \tag{7}$$

where K_2 is the equilibrium rate constant of pseudo-second-order adsorption (g/mg min). Integrating Eq. (7) for the boundary condition $t = 0$–t and $q_t = 0$–q_t, after rearrangement gives:

$$\frac{t}{q_t} = \frac{1}{K_2 q_{e2}^2} + \frac{1}{q_{e2}} t \tag{8}$$

The correlation coefficient for the pseudo-second-order kinetic model ($R^2 \geqslant 0.99988$) is higher than first-order, suggesting that the rate-limiting step may be a chemical sorption rather than a diffusion. These results imply that the adsorption system studied obeys to the pseudo second order kinetic model as shown in Table 2 and Fig. 6.

3.7. Competition between p-nitrophenol, o-chlorophenol and phenol

Fig. 7 shows that the maximum adsorption capacity was found to follow the order p-nitrophenol > o-chlorophenol > phenol. This can be explained by the

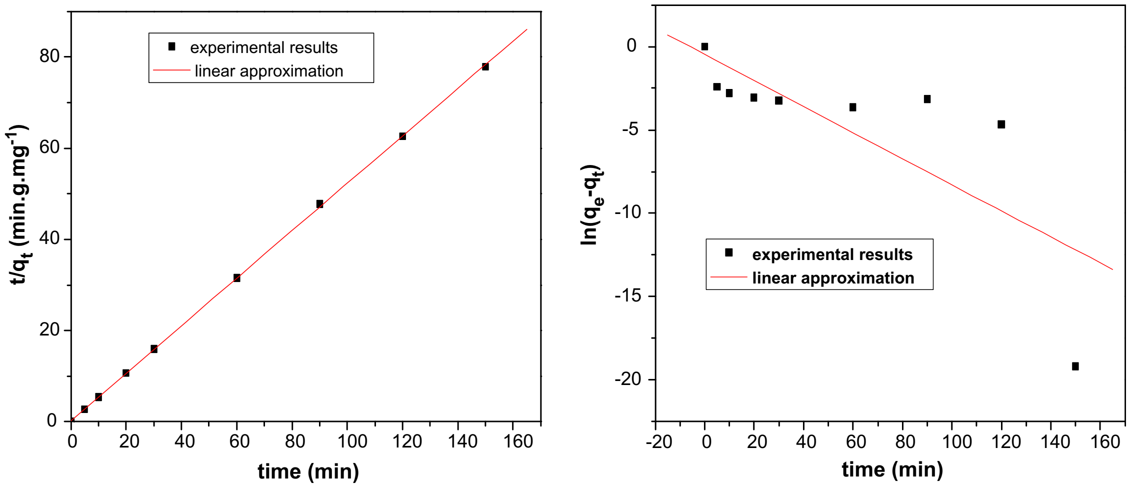


Fig. 6. Adsorption kinetics, (a) Pseudo second order kinetic; (b) pseudo first order kinetic: $V = 500$ rpm, pH = 4.17, $r = 1$ g/l, $d \leqslant 0.315$ mm, $T = 20 \pm 3$°C.

Table 2
Kinetics constants for adsorption of p-nitrophenol onto activated sawdust

Models	Constants	Coefficient
Pseudo-first-order kinetic	$K_1 = 0.07816$ (min^{-1})	$R^2 = 0.585806544$
Pseudo-second-order kinetic	$K_2 = 1.19450667$ (g mg^{-1} min^{-1})	$R^2 = 0.999880003$

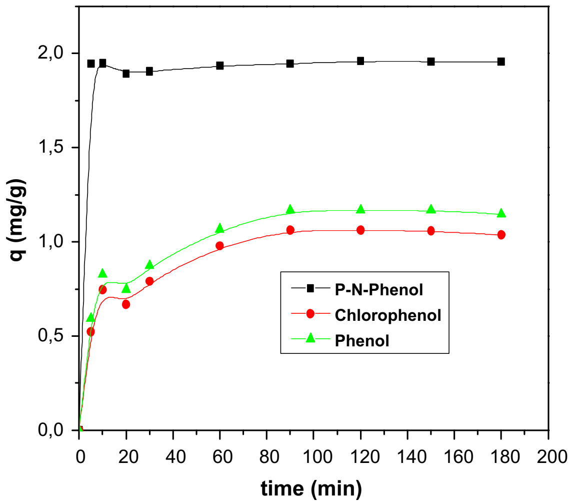


Fig. 7. Competition between phenols: $C_0 = 20$ mg/l, $V = 500$tr/min, $T = 22$°C, $d \leqslant 0.315$ mm, $r = 10$ g/l, pH = 5.79.

fact that the introduction of NO_2^- and Cl^- groups to phenol resulted in increased adsorption due to decreased water solubility [19]. Since p-nitrophenol is less soluble in water than o-chlorophenol and phenol, the sorption of the former is increased.

A donor-acceptor complex mechanism can also explain this result, since a carbonyl oxygen group on the carbon surface acts as the electron donor, whereas the aromatic ring of phenol acts as the electron acceptor [20]. The donor-acceptor complex mechanism is more pronounced in the case of p-nitrophenol as the presence of NO_2 is in favor of the formation of bond between the surface carboxylic groups and the electron poor of the aromatic ring of p-nitrophenol. A nitro group in phenol lowers electron density in the ring in comparison with phenol and p-nitrophenol is more adsorbed than phenol. o-Chlorophenol is also more adsorbed than phenol because of the electron withdrawing inductive effect of chlorine.

Adsorbates of different molecular size will be adsorbed to varying extent, depending on the availability of pores of appropriate size.

4. Conclusion

It may be concluded from the above observations that: (i) activated sawdust shows good adsorption capacity for the removal of p-nitrophenol from wastewater, (ii) the adsorption of p-nitrophenol was found to be dependent on pH, contact time, concentration and adsorbent dose, (iii) the equilibrium adsorption was best described by the Freundlich isotherm as indicated by high correlation coefficients, (iv) in the study kinetics of sorption, the pseudo-second-order model provides better correlation of the sorption data than the pseudo-first-order model, (v) the adsorption of phenols was found to follow the order p-nitrophenol > o-chlorophenol > phenol.

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