Experimental Study of Chlorophenol Elimination by Adsorption on Chemically Activated Wood Sawdust

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Abstract

The present work concerns an experimental study of the removal of chlorophenol by adsorption onto chemically activated wood sawdust.

The results confirmed the good retention capacity of sawdust for an organic pollutant, namely, Chlorophenol.

The effect of several parameters such as the contacting time, the initial concentration of the pollutant, the pH, the adsorbent dose, the isotherms and the kinetics were investigated. All the considered parameters had an effect on the adsorption capacity, but to different extents.

The results showed that the adsorption isotherms followed the BET model rather than Langmuir or Freundlich. The adsorption kinetics could equally well be represented by the 1st or 2nd order and also by the intraparticle diffusion models.

Keywords: *Surface diffusion; Chlorophenol; Wood sawdust, Adsorption.*

I. Introduction

With the increase of the populations and the industrial development, huge quantities of polluted wastewaters be they domestic or industrial, are systematically discharged directly or indirectly into the environment, without any prior and adequate treatment to remove harmful compounds. In most cases the effects are damaging not only to individual species and populations, but also to the natural biological communities. Consequently water pollution is a major global problem which requires ongoing evaluation and revision of water resource policy at all levels.

It has been claimed that water pollution is the leading worldwide cause of deaths and diseases [1], accounting for the deaths of more than 14,000 people daily [2]. Water pollution may be due to various reasons and one can agriculture runoff, Storm water runoff, leaking sewer lines, mining activities, foundries, accidental leaks and spills, animal wastes, etc.

Chlorophenols represent a particular group of priority toxic pollutants listed by the US EPA in the Clean Water Act and by the European Decision 2455/2001 EC. They are ubiquitous aquatic contaminants, originating even from natural sources [3].

Many examples of water treatment from chlorophenol are reported in the literature and one can cite, Removal of 4- chlorophenol by soybean peroxidase and hydrogen peroxide in a discontinuous tank reactor [4], Kinetics of p-chlorophenol wastewater treatment by UV/H_2O_2 oxidation.[5], Effect of 4-chlorophenol loading on acclimation of biomass with optimized fixed time [6], etc.

II. Experimental methodology

A. Principle

In order to develop, less expensive and effective process for the retention of chlorophenol, natural sawdust was proposed in the present study and was modified by a chemical treatment carried out at laboratory scale.

B. Preparation of Solutions and Support

- The adsorbent

The adsorbent was washed in a first step with distilled water to remove impurities, at least three times, and then dried in the sun exposure.

After drying, it was crushed, sieved to a diameter less than 0.315 mm and then kept in a desiccator. After screening, a part underwent the step of the following chemical treatments:

- **Treatment with sulfuric acid**

The adsorbent was mixed with sulfuric acid (H_2SO_4) at a concentration of 1 N, with a ratio of 1/10. The mixture underwent a thermochemical treatment at a temperature of 150°C, for 24 h. After that, we did wash the mixture with distilled water to remove any excess of acid. After filtration, it was mixed overnight with a 1% Sodium bicarbonate (Na_2CO_3) solution to eliminate the amount of residual acid. At the end, the support was dried to constant weight.

c) Solutions

All used chemicals were of analytical grade (Panreac PRS and PRS Chiminova). Chlorophenol solutions were prepared by dissolving the chlorophenol C_6H_5ClO in distilled water. All solutions of different concentrations were prepared by dilution of the 1g / l mother solution. The pH of the solution was adjusted with Nitric acid (HNO_3) (0.1M, 0.01M) and Sodium hydroxide (NaOH) (0.1M, 0.01M) using a pH meter (JENWAY 3510). The pH of solutions was not adjusted and its initial value was 5.79 ± 0.02. For the calibration curves in terms of chlorophenol it was necessary to prepare standard solutions (standards) from the chlorophenol solution of 1g/l, and the residual concentrations were read off by means of a spectrophotometer UV-visible (UV 160A SHIMADZU); Standards of concentrations 2, 5, 10, 20, 40, 60 and 80 mg / l were prepared.

3. Analysis chemical and experimental methodology

The Spectrophotometric analysis was based on the study of the change in absorption of light by a medium, according to the variation of the concentration of a constituent by measuring the relative absorption of the light with respect to that of a substance of known concentration. The light used in Spectrophotometric analysis was substantially monochromatic and when it reached a homogeneous medium, a fraction was reflected, and the other absorbed and the rest transmitted [7].

III. Results and Discussion

1. Effect of contact time

Adsorption is a transfer of contaminants from the liquid phase to the solid phase. The two phases were brought into contact, in batches, to study the pollutant solution (Chlorophenol) and the adsorbent considered (Sawdust form coal). The results are illustrated in the following figure 1:

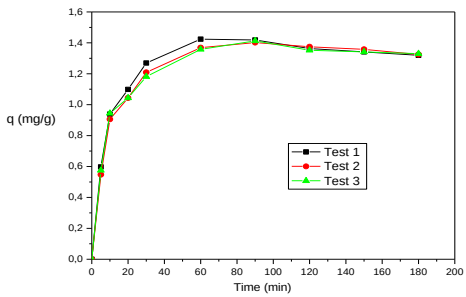

Figure (1): Effect of contact time on the retention of chlorophenol

The effect of contacting time on the capacity of removal of chlorophenol by chemically activated wood sawdust is shown in Figure 1 from which it can be seen that the adsorption for different was rapid in the initial stages and gradually decreased with the progress of adsorption until equilibrium was reached. The removal of chlorophenol increased with time and reached saturation in about 120-180 minutes. Initially the percentage removal of chlorophenol was high and increased rapidly to remain constant with time. Figure 1 shows that maximum percentage removal of chlorophenol was attained after about 120 minutes. The rate percentage of removal was higher at the beginning due to the large surface area of the chemically activated wood sawdust being available for the adsorption of the chlorophenol. With time the access to the remaining vacant surface sites would be more difficult due to repulsive forces between the solute molecules on the solid and bulk phases. For subsequent experiments, the contacting time was thus maintained for 180 minutes to ensure that equilibrium could be achieved. It should be noted that the retention q is simply the ratio of the difference of concentrations at times t and t + dt on the mass of the adsorbent. Three trials were performed and the results are quite similar and fluctuated around an average. The adsorption capacity increased with the contact time and this can be explained by the affinity of the carrier with respect to chlorophenol. The adsorption efficiency was better for a contact time of 90 min to 120 min.

2. Effect of solid-liquid ratio

In order to examine the influence of solid / liquid ratio on the retention capacity of the chlorophenol, the initial amount of support was varied while keeping the volume of the solution constant. Four values were considered as shown in Figure 2:

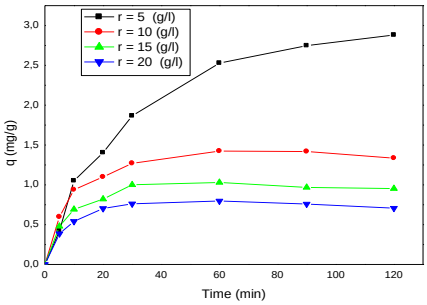

Figure (2): Effect of solid / liquid ratio on the retention of chlorophenol

Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given concentration of the adsorbate. The adsorption studies of chlorophenol on chemically activated wood sawdust was done at 25°C temperature by varying the quantity of adsorbent from 5 g/l to 20 g/l while keeping the volume of the metal solutions constant at pH 5.794. When the adsorbent dosage was increased from 5 to 20 g/l the amount adsorbed per unit mass of adsorbent decreased considerably as shown in Figure 2. The decrease in unit adsorption with increase in the dose of adsorbent was due to the increase in active sites on the adsorbent and thus making easier the penetration of the chlorophenol into the adsorption sites.

3. Effect of initial concentration

The initial concentration of the organic pollutant has an important influence on the retention capacity of the solid support and in order to study its effect several values were taken as shown in Figure 3:

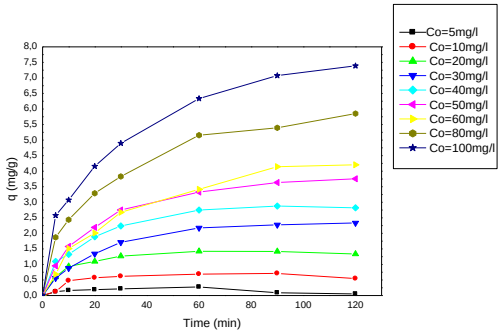

Figure (3): Effect of initial concentration on the retention of chlorophenol

According to the previous figure increasing the initial concentration of organic pollutant caused a significant increase in the adsorption capacity and a remarkable decrease in percentage removal (performance). This can be explained by the fact that when the concentration in the solution of the chlorophenol is high, there will be more molecules of chlorophenol diffusing to the surface of the support sites, hence increasing their retention. The retention rate is important for low levels and continues to rise until the onset of the plateau indicating saturation. This can be explained by exhaustion of all existing active sites on the surface of medium by the molecules of the chlorophenol.

3.4 Effect of pH

The pH of the solution is important in the adsorption phenomenon. For this five pH values were considered as shown in Figure 4.

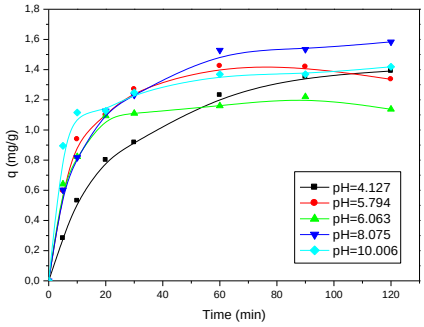

Figure (4) Effect of pH on the retention of chlorophenol

The effect of pH on the adsorption of chlorophenol on chemically activated wood sawdust is presented in Figure 4. It shows that the adsorption of the chlorophenol in the pH range of 4.127 to 10 varied between 1 and 1.6 mg/g. The percentage removal of chlorophenol was at minimum at the pH 4.127 and increased with further increase in pH. At pH value lower than 6, the adsorption capacities were found to be low due to the competitive adsorption of HO_3^+ ions and chlorophenol for the same active adsorption sites. As the pH increased, the adsorption surface became less positive and therefore electrostatic attractions between the chlorophenol and chemically activated wood sawdust surface was likely to increase. The adsorption capacity increased

by increasing the pH to a certain value and then decreased. The adsorption capacity reached its maximum at pH equal to 8.075 and then gradually decreased for pH value of 10.006, explaining this phenomenon.

3.5 The adsorption isotherms

An adsorption isotherm is the variation in the quantity q of compound adsorbed onto a solid depending on its concentration in the contacting fluid at a temperature T. To quantify the adsorption capacity of chemically activated wood sawdust for the removal of chlorophenol from aqueous solution, the Langmuir, Freundlich and BET isotherm models were tested. A trial and error procedure was used to determine the three isotherms parameters by minimizing the respective correlation coefficient between experimental data and isotherms shown on Table 1.

Table (1): The kinetic constants and correlation factors of different adsorption isotherms chlorophenol on sawdust.

Type of isotherm	Linearization of equations	Constants	R
BET [8]	$\frac{c_e}{q_e(c_0-c_e)}=\frac{1}{q_m k}+\frac{k-1}{q_m k}\frac{c_e}{c_0}$	k=-2.5115 q_m=0.0054	0.9498
Langmuir [9]	$\frac{C_e}{q_e}=\frac{C_e}{b}+\frac{1}{a\,b}$	*a* = -0.679 *b*= -21.513	-0.403
Freundlich [9]	$Ln(q)=\ln(K_f)+\frac{1}{n}\ln(C)$	K_f = 0.0178 1/*n*= 1.9818	0.8322

From Table 1, the BET adsorption isotherm model led to the best fit as indicated by the highest R values compared to the Freundlich and Langmuir adsorption isotherm models. So chemically activated wood sawdust was found to have a relatively good adsorption capacity of 20 mg/g and this indicated that it could be considered as a promising material for the removal of chlorophenol from aqueous solutions.

3.6 Study of the kinetics of retention chlorophenol

Knowledge of the kinetics of adsorption has considerable practical interest in the efficient implementation of an adsorbent in an industrial operation and knowledge of the factors was optimized to produce or improve an adsorbent leading to the kinetic. It is recognized that the dynamic process of adsorption, both in the gas phase and in the liquid phase also can be of one of the thrre models shown by Table 2:

Table (2): Parameters of kinetic models studied

Kinetic Models	1st order [10]		2nd order [10]		Intra particle diffusion [11]	
Constant	K_1 (mi)	R	K_2 (g/mg. min)	R	K_{int} (mg/g. mi ^{½})	R
Value	-0.10	-0.987	0.2492	0.99	0.23	0.98

From linear regressions, it could be concluded that the retention of chlorophenol on activated sawdust was not represented by second order kinetics. In fact the three models could equally well represent the kinetics since the three correlation factors were very close, as shown by Table 2:

Conclusion

The present study showed that chemically activated wood sawdust, an agricultural waste material, can be used as an adsorbent for the removal of chlorophenol ions from aqueous solutions. The BET isotherm equation fitted very well the equilibrium data, confirming the different layers of adsorption capacity of chlorophenol onto chemically activated wood sawdust. Experimental Study of the elimination of Chlorophenol by adsorption on Chemically Activated Wood Sawdust showed that the all considered operating parameters had an effect on the retention capacity of chlorophenol by activated sawdust.

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