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Determination of Uptake and Release of 2,4-Dichlorophenol on the Nigerian Clay Soil using Gas-Liquid Chromatography

E. Augustine Ofomaja*, O. Bridget Ofomaja and A. Stephen Uzoekwe

Department of Industrial Chemistry, Faculty of Physical Science, University of Benin, Benin City, Nigeria.

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ABSTRACT

The uptake and release of 2,4-dichlorophenol on Nigerian clay soil was studied by introducing varying concentrations of the chlorophenol in 0.01 M aqueous calcium chloride solution at pH 4.5 into pretreated clay (0.6% OM) samples. The clay soil was treated with hydrogen peroxide followed by varying concentrations of sulphuric acid (0.1, 2.0, 4.0 and 6.0 N). The uptake of 2,4-dichlorophenol was higher for treated clay soil samples with lower cation exchange capacity. The sorption isotherm plots were non-linear, suggesting that sorption of sorbate onto sorbent is by adsorption mechanism and that charged species are involved. The sorption process was well described by the Freundlich isotherm. Clay soil samples with higher cation exchange capacities released smaller amounts of the adsorbed chlorophenols, therefore retaining close to half of the adsorbed amount due to strong adsorption of the charged species on the clay surface. The clay soils with lower cation exchange capacities released higher amounts of the adsorbed chlorophenols, due to the higher contribution of hydrophobic interaction between organic matter and hydrophobic sites on the clay surface.

KEYWORDS

2,4-dichlorophenol, adsorption, sulphuric acid treatment, hydrophobic interaction, desorption.

1. Introduction

Chlorophenols are among several organic compounds classified by the U.S. Environmental Protection Agency as 'priority pollutants'[1]. Chlorophenols represent one of the most challenging classes of pollutants to be removed from waste streams and ground waters[2] and are difficult to biodegrade (they can only biodegrade under anaerobic conditions); this contributes to their persistence in soil.

The fate of chlorophenols in the soil environment and their removal from aqueous waste streams is complicated by their low solubility, ability to ionize, low vapor pressure, and tendency to undergo oxidation and oxidative polymerization to humic and fulvic acid-type products[3–7].

The removal of such compounds at low levels constitutes a difficult problem. Among methods employed are either destructive oxidation with ozone[8] and hydrogen peroxide[9,10], or adsorption onto porous solids such as activated carbon[11,12], Fly ash[13] and clays, either untreated or pillared[14–20]. Among the porous solids, activated carbons are the most effective and can be regenerated by thermally desorbing or combusting the toxicant in air, but substantial fraction of the carbon is lost with each oxidation cycle. This loss of adsorbent is a major economic consideration in any large-scale remediation application[21].

The retention of hydrophobic organic compounds in sediments and soils is often attributed to partitioning of hydrophobic organic molecules into organic matter. Hassett *et al.*[22] studied hydrophobic organic compound sorption by sediments and soil materials with a wide range of organic carbon contents and reported that organic matter could mask the contribution of minerals to sorption of hydrophobic organic compounds.

It has been found that clay minerals are the dominant adsorbents of nonionic and neutral hydrophobic compounds in subsoil and sediments that contain less than 1% organic carbon[22]. Clays may also contribute significantly to the sorption of nonionic and neutral compounds in surface soils[23].

In the present investigation, a local Nigerian soil clay will be acid treated with different concentrations of sulphuric acid and used in the adsorption of 2,4-dichlorophenol from aqueous solution. The physicochemical properties of the 2,4-chlorophenol are: molecular weight 163, solubility in water 4500 mg dm^{-3}, pKa 8.15, octanol-water partition coefficient, (K_{ow}) 2.9. The effect of hydrogen peroxide and sulphuric acid treatment on 2,4-dichlorophenol sorption and desorption and the mechanism of interaction between the 2,4-dichlorophenol and the treated clay soils were examined.

2. Experimental

2.1. Sample Preparation

Soil clay was obtained from Edo state of Nigeria. Samples were treated to isolate the <2 μm clay fraction while still in a field moist condition by repeated settling and decantation. The mineralogical assemblage of the clay soil was investigated using a DIANO 2100*E X-ray diffractometer using Copper anticathode (λ = 1.54Å). XSPEX version 5.41 software was employed in the interpretation of the diffractogram obtained from the analysis. The organic matter was destroyed with hydrogen peroxide as described by Bhattacharyya[24] .

Suspensions of the soil clay were flocculated with an excess of calcium chloride and washed to remove anions. The sample was divided into five portions, which were treated under mechanical stirring with 100 mL of 0.5, 1.0, 2.0, 4.0 and 6.0 N solution of sulphuric acid, for 1 hour under reflux and were washed to remove excess acid. The clays were designated M0.5, M1.0, M2.0, M4.0 and M6.0.

2,4-dichlorophenol was purchased from BDH limited and used without further purification. The varying concentrations

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* To whom correspondence should be addressed. E-mail: aus_ofomaja@yahoo.com

(100, 150, 200, 250 and 300 mg dm^{-3}) were prepared in 0.01 M aqueous calcium chloride solution.

2.2. Surface Area

The specific surface area was determined by the method described by Hajajji[25]. In this procedure, 5 mg suspension was added to seven beakers containing methylene blue of concentrations ranging from 0.42–4.9 × 10^{-6} mole dm^{-3}. The mixtures were stirred at interval and left overnight. The clay suspensions were centrifuged and the clear supernatant analysed for the concentration of methylene blue left at 665 nm. The amount of methylene blue left in solution was plotted against the amount of methylene blue added. The optimum point of flocculation was identified from the plot and used in computation of the surface area as shown below:

$$\text{Surface area (m}^2\text{ g}^{-1}) = M_f \times A_m \times 6.02 \times 10^{-2},$$

where M_f is the meq of methylene blue adsorbed per 100 g of clay when the surface is covered (point of optimum flocculation), and A_m is the area per molecule in Å^2 on the surface.

2.3. Cation Exchange Capacity

Cation exchange capacity was measured by the method described by Lalithambika[26]. Folowing this method, 1.0 g of the clay soil was saturated with 1.0 M ammonium acetate solution adjusted to pH 7.0 using a pH meter (WTW pH Meter 320, Germany). The soil clays were then refluxed with magnesium oxide solution and the liberated ammonia was collected in boric acid solution containing mixed indicator. This solution was titrated against standard HCl (standardized using Na_2CO_3) and the end point was indicated by the colour change from green to pink.

2.4. Adsorption/Desorption Experiment

The batch adsorption experiments were carried out in 50 mL glass centrifuge tubes where 0.3 g of clay and 25 mL of the 2,4-dichlorophenol solutions (100–300 mg dm^{-3}) were added. The centrifuge tubes were subsequently capped and shaken in a wrist-action shaker for 24 hours at 25°C. The suspensions were centrifuged at 10 000 rpm for 30 min and analysed by gas chromatography.

Desorption experiments were then carried out on the remaining soil by adding 25 mL of 0.01 M calcium chloride. The centrifuge tube was capped and shaken for 6 hours. After centrifugation, the supernatant was taken for determination of 2,4-dichlorophenol equilibrium concentrations. Each sample was run in triplicate.

2.5. Analysis of 2,4-Dichlorophenol by Gas-Liquid Chromatography

2,4-dichlorophenol was analysed by gas-liquid chromatography (GC) on HP-17 10 m × 0.53 nm capillary column. The analyses were carried out on a HP 5890 Series II gas-chromatograph equipped with a flame ionization detector and interfaced with an HP 3365 Chem Station. The area ratios were converted to mole ratios for quantitative determination by using internal standard calibration curves constructed from known mixtures. Trichlorophenol was used as internal standard. The amount of 2,4-dichlorophenol adsorbed onto the clay was calculated by difference.

3. Results and Discussion

3.1. Properties of Clay Soil

The mineralogical assemblage of the clay soil showed that the clay consisted of illite (61%), smectite (11.5%), quartz (24%) and hematite (2.5%) and has percentage composition: SiO_2 (58.3%), Al_2O_3 (17.5%), MgO (9.7%), CaO (2.34%), Na_2O (0.6%) and K_2O (4.5%) as determined by atomic absorption spectrophotometer. The organic matter content was 1.7% before treatment and 0.6% after treatment.

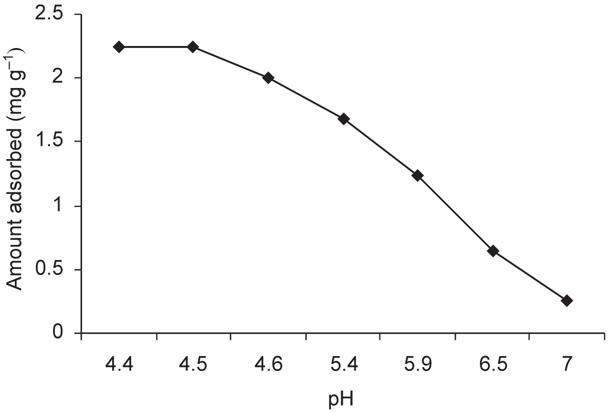

Figure 1 Amount of chlorophenol adsorbed at different pHs.

3.2. Physicochemical Properties of Acid-treated Clays

The changes in physicochemical properties of the clay after acid treatment were evaluated by monitoring the extent of modification of surface area and cation exchange capacity after acid activation. Fig. 2 shows the relationship between acid concentration, surface area and cation exchange capacity. Both surface area and cation exchange capacity increases with increasing acid concentration between the 0.5 to 2.0 N acid treatments, while both parameters decreases in value between the 4.0 to 6.0 N acid treatments. Increases in surface area through the leaching of Al in clay minerals have been reported by various authors[27–30]. The increase may also be due to the removal of surface coating materials such as sesquioxides[31] and exposure of internal surfaces, which were formerly closed. The reduction in value of these properties after initial increases have been explained by Breen[32] to result as the product takes on the properties of amorphous silica, which has been identified as the final product of acid leaching.

3.3. Uptake of 2,4-Chlorophenol on Sulphuric Acid-treated Clays

To investigate the possibility of coulombic interactions involved in the binding of 2,4-dichlorophenol, the pH dependency of adsorption by clay was investigated (results are shown in Fig. 1). As the pH decreases, the adsorption increases and the adsorption at pH 4.5 was found to be 10 times that of the adsorption at pH 7.0. Therefore all experiments were carried out at pH 4.5 using a pH meter (WTW pH meter 320, Germany).

Data obtained for the uptake of 2,4-dichlorophenol from solutions of different concentrations by sulphuric acid-treated clays are shown in Table 1 (preliminary kinetic experiments demonstrated that adsorption equilibrium was reached within 20 hours). Uptake of chlorophenol from all solutions used were highest for clays treated with 0.6 N and 0.5 N sulphuric acid solution, while clays treated with 1.0 N and 2.0 N sulphuric acid solution gave the least uptake for all chlorophenol solutions used. These trends can be explained by examining the changes in physicochemical properties of the clay surfaces, the sorption mechanism and the nature of the adsorbed species.

Sulphuric acid treatment of the clay soil at different acid concentrations modifies both surface area and cation exchange capacity of the clay soil to different extents as shown in Fig. 2.

Table 1 Uptake of 2,4-dichlorophenol from solutions of different concentrations onto clay soils pretreated with H_2SO_4 solutions of different concentrations.

Sample	2,4-dichlorophenol solution (mg dm^{-3})					CEC (meq 100 g^{-1})
	100	150	200	250	300	
M0.5	3.50	1.86	2.00	2.70	3.60	33.0
M1.0	7.50	4.90	5.00	7.00	8.30	46.0
M2.0	9.90	7.15	7.00	10.00	11.90	51.0
M4.0	14.00	7.71	9.00	12.50	19.20	41.0
M6.0	18.00	8.08	11.25	14.50	21.70	27.0

Table 2 Values of Freundlich adsorption constants and R^2 values of 2,4-dichlorophenol isotherm.

Sample	n_f	K_f (mol/g) (1/mol)^{nf}	R^2
M0.5	0.78	0.209	0.9985
M1.0	0.85	0.17	0.9978
M2.0	0.87	0.083	0.9996
M4.0	0.84	0.141	0.9996
M6.0	0.79	0.355	0.9992

Maximum values for cation exchange capacity and surface area were observed for sample M2.0 and lower values were observed for samples M0.5 and M6.0. Comparing the trend in the uptake of 2,4-dichlorophenol on each clay soil against the cation exchange capacities (Table 1), it is observed that the highest uptake of 2,4-dichlorophenol from solution is observed for clay soils with low cation exchange capacity values. This suggests that negatively charged sites on the clay surface affects the sorption of adsorbate molecules, which may likely be charged species.

Two general mechanisms for the uptake are possible, (i) the partition mechanism and (ii) the adsorption mechanism. First is the partition mechanism, where the uptake of organic molecule has no relationship with the specific sites on the soil but with organic solubility[33] or organic molecule interacting with charged siloxane surfaces that are relatively hydrophobic[34]. In the adsorption mechanism, the organic molecule is adsorbed on specific adsorption sites via hydrogen bonding, charge transfer, ion exchange or ligand exchange[35, 36].

The sorption isotherms of the 2,4-dichlorophenol uptake on clay soils are shown in Fig. 3. From the plot, it can be seen that the curves can be described as non-linear isotherms. Several authors have reported the non-linear behaviour for the uptake of chlorophenols on soils and clays[37–39]. The sorption behaviours of organic compounds from water to soil phase have been expressed by either the linear and the non-linear equation. Where the non-linear equation is applicable, the adsorption mechanism is the controlling factor for organic molecule sorption. But where the linear equation applies, the partition process is regarded as the major sorption mechanism, which assumes the soil as the solvent.

The non-linear isotherms in Fig. 3 vary in their degrees of curvature. Samples M6.0 and M0.5, although non-linear, tend to be more linear in nature than samples M4.0, M2.0 and M1.0. The degree of curvature increases from M6.0 < M0.5 < M4.0 < M1.0 < M2.0. Therefore we speculate that partition mechanism reduces in importance as the main sorption mechanism as the degree of curvature of the isotherm plot increases. Adsorption mechanism is therefore more pronounced in samples M4.0, M2.0 and M1.0, while a mixed mechanism may exist in samples M6.0 and M0.5.

The sorption process was well fitted to the Freundlich isotherm curves and values of Freundlich constants n_f, K_f and R^2 for the plots are shown in Table 2. The Freundlich equation is as shown below:

$$n = K_f C_{eq}^{n_f} \qquad (1)$$

$$\log n = \log K_f + n_f \log C_{eq} \qquad (2)$$

with n = adsorbed amount (mg g^{-1}) and C_{eq} = equilibrium concentration (mg dm^{-3}). The empirical parameters n_f and K_f (K_f (mg g^{-1}) (1 mg^{-1})^{nf}) were derived from the slope and the intercept. The non-linearity of the isotherm is indicated by n_f[40]. From Table 2, it is observed that values of n_f for all samples are less than 1, indicative of L-type isotherm as described by Giles *et al.*[40]. The L-type isotherm expresses the low competition of the solvent

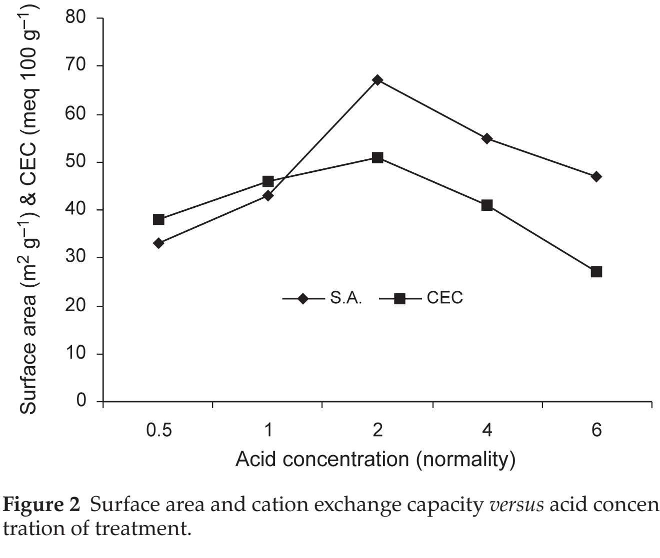

Figure 2 Surface area and cation exchange capacity *versus* acid concentration of treatment.

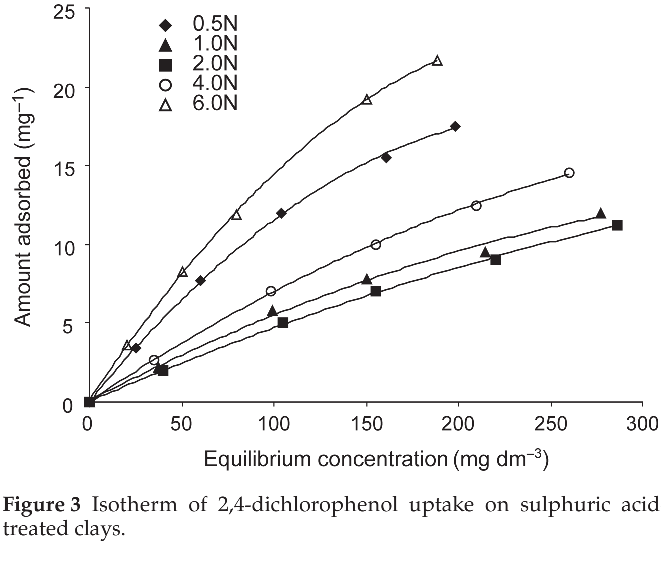

Figure 3 Isotherm of 2,4-dichlorophenol uptake on sulphuric acid-treated clays.

Table 3 Amounts of 2,4-dichlorophenol in equilibrium, adsorbed, desorbed with water and remaining adsorbed in aqueous suspension of H_2SO_4-activated clays (n = 3) *.

Clay sample	Equil. Conc. (%)	Adsorption (%)	Desorption in water (%)	Bound residues (%)
M0.5	25	75	67(78.6)	16
M1.0	37	63	36(57.1)	27
M2.0	40	60	31(51.1)	29
M4.0	35	65	40(61.5)	25
M6.0	20	80	63(78.8)	17

* Triplicate experiments. Listed are the amounts with regard to the initial concentration and, inside the brackets the amounts with regard to the adsorbed amount.

molecules with the adsorptive molecules for the adsorption sites. As the surface negative charges reduces (i.e. lower cation exchange capacity, for samples M0.5 and M6.0) the partition mechanism becomes important and both adsorption and partition mechanism are in operation. Whereas when surface negative charges increase (i.e. higher cation exchange capacity, for samples M1.0, M2.0 and M4.0) adsorption mechanism becomes predominant.

The species believed to be active in the partition mechanism is the neutral form of 2,4-dichlorophenol at low pH, while in the adsorption mechanism the species are suspected to be i) the phenolate ions, which have been identified to be adsorbed on Ca-montmorilonite and Ca-kaolinite[30]. The adsorption of the phenolate ion has been found to be relatively independent of pH changes (4.7–7.5) of clay suspension[41,42]; ii) the phenolate ion pair, e.g. Ca-chlorophenol$^+$. The formation of the ion pair or complex with metal cation is as follows:

$$Ca^{2+} + \text{Chlorophenol}^- \longrightarrow \text{Ca-Chlorophenol}^+ \quad (3)$$

(The Ca^{2+} ions are those on the Ca-saturated clay).

McGill and co-workers[36] studying the influence of clay mineralogy on Ca-chlorophenol$^+$ sorption concluded that internal surface area was not important in adsorption. They found that sorption of Ca-chlorophenol$^+$ on Kaolinite and montmorilonite were not much different in terms of amount of chlorophenol adsorbed. Therefore, Ca-chlorophenol$^+$ adsorption occurs mainly on the edge and opening wedge at the edge (external surface). Since the phenolate species are among the two charged species that can be adsorbed on the clay soil, and that presence of these species are relatively independent of pH, increase in negative charge on the clay surface will cause the Columbic repulsion and reduce the amount of chlorophenol adsorbed on the clay surface. Reduction in negative charge (i.e. reduction in cation exchange capacity) will lead to increased chlorophenol uptake (as shown in Table 1). This may explain the higher sorption amounts on sulphuric acid-treated clay soils with lower cation exchange capacity than those with higher cation exchange capacity.

3.4. Desorption Results

The amounts of 2,4-dichlorophenol desorbed from the clays into water can be obtained using method adapted by Albanis *et al.*[43], from the calculation of mass balance of 2,4-dichlorophenol based on the following equations:

[Initial amount] = [Free amount] + [Adsorbed amount].

The adsorbed amount could be analysed as follows:

[Adsorbed amount] = [Desorbed amount with water] +
[Bound residues].

The permanent adsorbed amount is calculated from the difference between adsorbed amount and the amount desorbed in water.

The mass balances for the removal by adsorption as well as the desorption of 2,4-dichlorophenol from the acid-treated clay soils are summarized in Table 3 (Preliminary kinetic experiments demonstrate the desorption equilibrium was reached within 6 hours). The amounts of 2,4-dichlorophenol desorbed into water from each of the sulphuric acid-treated clay soils were found to be higher for samples M6.0 and M0.5 than for samples M1.0, M2.0 and M4.0.

It has been shown that chlorophenol sorption on soils is nearly reversible at low pH values, the ionized forms have been found to show only about 50% desorption because it is more strongly bound to the surface[44]. Values for desorption percentage indicates that the resistance to desorption was higher for samples M1.0, M2.0 and M4.0, which also had higher cation exchange capacities values and the sorption isotherms were more nonlinear. This suggests that charged forms of the 2,4-dichlorophenols (adsorption) would have been the predominant species adsorbed on the surface. Samples M6.0 and M0.5, on the other hand, with lower cation exchange capacities and more linear sorption isotherms had 67% and 63% desorption. These values show a higher amount of desorption, suggesting that hydrophobic mechanism may be involved in the binding of the 2,4-dichlorophenol molecules to the clay, thereby releasing a higher amount into solution[45].

4. Conclusion

Uptake and desorption of 2,4-dichlorophenol between solution and soil are controlled by surface properties produced by treatment of clay soils with sulphuric acid activation of different concentrations. The species involved in the sorption process were the non-charged species, the negatively charged species and the phenolate ion pair. The sorption process was increasingly controlled by the adsorption mechanism as the cation exchange capacity increased but sorption was more likely a mixed mechanism at lower cation exchange capacity values.

The desorption of 2,4-dichlorophenol from the clays increased with increase in values of cation exchange capacities and increased non-linearity of 2,4-dichlorophenol isotherm curve. This may suggest binding of the charged form of 2,4-dichlorophenol molecules. The decrease in cation exchange capacities and slight non-linearity of 2,4-dichlorophenol isotherm curve led to decreased desorption, suggesting hydrophobic binding along with binding of charged 2,4-dichlorophenol molecules.

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