

**ADSORPTION OF 2- CHLOROPHENOL AND
2, 4 DICHLOROANILINE ON SILICA
AND
ADSORPTION AND DESORPTION OF
PHOSPHATE ON KAOLINITE**

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T.H.N.M.KARUNATHILAKE

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T.H.N.M. Karunathilake
Department of Chemistry
University of Peradeniya
Peradeniya
Sri Lanka

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2-Chlorophenol, 2,4-dichloroaniline and phosphate which come from herbicides, pesticides and industrial effluents contaminate water bodies and cause adverse effects on living beings. The objective of this study was to investigate the influence of adsorption of 2-chlorophenol and 2,4 dichloroaniline on silica and the influence of adsorption and desorption of phosphate, on kaolinite under different experimental parameters. Effects of pH, ionic strength, initial concentration and contact time were studied for the adsorption of 2-chlorophenol and 2,4 dichloroaniline on silica. Adsorption and desorption studies of phosphate on kaolinite were studied as a function of pH, initial phosphate concentration and contact time. Adsorbed and desorbed amount of phosphate was determined using the Phosphovanadomolybdate method.

The effect of pH was determined in the pH range of 2 to 12. The highest adsorption capacities for 2-chlorophenol and 2,4 dichloroaniline were observed around pH 6 and 7 respectively. After the treatment the pH of the medium was higher in the acidic region and vice versa in the basic region. $-H_2O$ molecules coming to the solution as a result of surface interactions of 2-chlorophenol or 2,4 dichloroaniline with silanols lower the solution pH in the acidic region. Formation of bidentate complex releases $-HCl$ to the medium and lowers the solution pH in the basic

region. Further, hydrogen bond formation between neutral 2-chlorophenol or 2,4 dichloroaniline molecules with surface silanols enhances the adsorption capacity.

Ionic strength of the medium was inversely proportional to the adsorption amount. Competition between the counter ions and the formation of the electric diffuse double layer retard the adsorption process. Surface charge of the adsorbent also influenced the adsorption amount. Outer sphere complexes were predominant during the adsorption process of the both systems.

Effect of concentration on adsorption was studied at pH 6 for 2-chlorophenol and at pH 7 for 2,4 dichloroaniline. Linear behavior of the adsorbed concentration and the equilibrium concentration was observed. Saturated condition was not observed due to capillary condensation effect of silica. The adsorption data fitted well into the Freundlich adsorption isotherm model in both the systems. Regression coefficient values were greater than 0.9 in all cases. This further confirms that adsorption processes are multilayeric over a heterogeneous adsorbent surface.

Adsorption kinetics was evaluated at pH 6 for 2 chlorophenol and at pH 7 for 2,4 dichloroaniline. The rate of adsorption was rapid initially and then slowed down gradually until it attained an equilibrium. Equilibrium condition was reached after 5 hours for 2-chlorophenol and after 3 hours for 2,4 dichloroaniline. It was found that adsorption of 2-chlorophenol and 2,4 dichloroaniline on silica was of first order according to the integrated rate law and Lagergren rate equation.

Interactions between silica and 2-chlorophenol or 2,4 dichloroaniline were investigated by means of Fourier Transform Infrared (FTIR) spectroscopy. Appearance of new peaks and reduction of intensities of the peaks gave evidence of the adsorption mechanism. In both systems reduction of peaks intensities in the region of $3000 - 3600 \text{ cm}^{-1}$ proved the surface interactions with $-\text{OH}$ groups. Conspicuous changes of the peaks were observed in the range of $800 - 1700 \text{ cm}^{-1}$. Changes in that region showed the presence of $-\text{C}-\text{Cl}$, $-\text{C}=\text{C}-$, $-\text{C}-\text{O}$, $-\text{C}-\text{N}$ silica under different experimental conditions. Shifting and broadening of the peaks were observed at different pH conditions. However the reduction of intensities and the peak broadening in the region of $1000-1400 \text{ cm}^{-1}$ clearly showed the interactions with the surface $-\text{Si}-\text{O}$ and $-\text{Si}-\text{O}-\text{Si}-$ groups. These changes were similar at all experimental conditions.

Influence of pH on the adsorption of phosphate on kaolinite was studied in the pH range of 1-12. It was found that the adsorption capacity increased from pH 1 to 3 and decreased from pH 3 to 12, showing the maximum capacity, from pH 3 to 5. Percent adsorption was inversely proportional to the initial phosphate concentration. Adsorbed concentration increased linearly at low phosphate concentrations and it reached equilibrium when the equilibrium phosphate concentration was 0.80 mg dm^{-3} . Experimental results fitted well with the Langmuir isotherm model confirming the monolayeric and chemisorption process.

Desorption was maximum in the pH range of 5 to 7. It was higher when increasing the solution to clay ratio at different time intervals than at constant solution to clay ratio. Surface charge of kaolinite and the interactions between phosphate and ~~kaolinite~~ govern the desorption capacity. Desorption reaction was of second order at pH 5 and 7.

Intensities of the bands in FTIR spectrum decreased with disappearing of peaks at 3555 cm^{-1} , 3473 cm^{-1} and 3434 cm^{-1} upon the adsorption of PO_4^{3-} . Deprotonated phosphate ($H_2PO_4^-$) showed a major peak at 1074 cm^{-1} and weak peaks at 1160 cm^{-1} , 940 cm^{-1} and 870 cm^{-1} . The dominant phosphoric acid H_3PO_4 species showed doublets at 1179 cm^{-1} and 1006 cm^{-1} . Interaction between hydroxyl of the Al-OH group and the phosphate shifted peak positions in the treated sample.