

ADSORPTION OF ORGANIC POLLUTANTS FROM WASTEWATER ONTO ORGANOCCLAY IN BATCH ADSORBER

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Abstract: Batch experiments were carried out to obtain the adsorption isotherms of phenol, *p*-nitrophenol and salicylic acid (single, binary and ternary systems) onto modified clay (organoclay). This clay was prepared from blending of local bentonite with quaternary ammonium. The organoclay was characterized by XRD and total organic carbon. The XRD diagram Also indicating that the basal spacing of 13.6 Å for natural clay increased to 18.2 Å for modified clay. The total organic carbon is found to be (20.3%) for modified clay more larger than natural clay (1.2%). The Freundlich isotherm model fitted well the adsorption data for each solute in a single system, whereas the combination of Langmuir-freundlich model was used in binary and ternary systems. A batch adsorber model was used to determine the pore and surface diffusion coefficients for each solute. The results show that salicylic acid is being adsorbed faster than phenol and *p*-nitrophenol, and the adsorption process was controlled by surface diffusion.

Keywords: Batch adsorber, Freundlich model, Mathematical model, Phenolic compounds.

INTRODUCTION

There were a wide range of pollutants released from industries including: Phenolic compounds, sulfides, suspended solids, toxic metals, acids, alkaline and biochemical oxygen demand. Methods are commonly used for their removal involve: biological degradation, chemical oxidation, solvent extraction, physical stripping and adsorption process. Adsorption techniques are widely used for removing pollutants from water, which can be carried out in batch wise or continuous operation.

Activated carbon is an adsorbent that is commonly used in the removal of organic compounds from water, but it is an expensive and non-selective adsorbent. Also, its pores susceptible to blocking by organic hydrocarbons of low solubility. Alther, (2001), Sulaymon and Ahmed, (2008), Sulaymon *et al.*, (2009).

Clay can be considered as an alternative adsorbent due to its effectiveness in removing organic compounds from water and its abundance, availability and low cost, but, clays are not capable of removing poorly water soluble and nonionic organics from water due to hydration of

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inorganic exchangeable ions present on their surfaces and the polar nature of the Si-O groups which impart a hydrophilic nature to the surface of clays. Therefore, researchers have attempted to modify the hydrophilic property of the clay by replacing the inorganic cations present on the surfaces and interlayer spaces of clays by a variety of organic cations, and thus changing the hydrophilic nature of clays to organophilic (Kowalska *et al.* 1994). In addition, exchanged organic cations act to keep open aluminosilicate layers of the clays, thus resulting in greater interlayer spacings that do not swell in the presence of water. The clays so formed are called organoclays. As a result, organoclays have become excellent sorbents for hydrophobic nonionic organics (Boyd *et al.* 1988).

For a system containing more than one adsorbable species (multicomponent system), the concentration of each species shifts relative to one another as the fluid travels. The shift, however, soon stabilizes to form the concentration profiles.

Mortland *et al.* (1986) showed that phenol and several of its chlorinated congeners were sorbed by modified clay. The results show phenol itself was not sorbed significantly by these complexes, but trichlorophenol was strongly sorbed. In other words, as hydrophobicity of the molecule increased, sorption increased.

Sharmasarkar *et al.* (2004) demonstrated that organoclay can be used for the containment of environmental pollutants originating from waste sites or accidental spills. A batch study was conducted using organoclays produced from a montmorillonite and three types of organic cations. The results indicated that organoclays with smaller cations had greater hydrocarbon retention. The ability of sorption of BTEX followed the order of TMPA > TMA > HDTMA organoclays.

Piyamaporn *et al.*, (2005) studied the removal of cationic and azo dyes by montmorillonite and organo-clays in a batch system. Methylene blue represents a cation dye while methyl orange was chosen as an anionic dye. The batch experiments showed that the methylene blue adsorption rate with the precursor montmorillonite was higher than that with the organic- modified clays while the methyl orange adsorption results were opposite.

Kim *et al.*, (2005) investigated single and bi-solute sorption and desorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol onto montmorillonite modified with hexadecyltrimethylammonium (HDTMA) using multi-step and desorption procedure. The results show that in bi-solute competitive systems, sorption affinity of both chlorophenols was reduced compare that in its single-solute system due to the competition between solutes.

The objective of the present study is to prepare organoclay from natural clay to adsorb phenol, p-nitrophenol and salicylic acid in single, binary and ternary systems from their aqueous solutions in batch process. Also, to investigate competitive adsorption of organic compounds from water onto organoclay as adsorbent in batch adsorber.

MATHEMATICAL MODEL

In the present study a mathematical model for batch adsorption will be employed following the assumptions adopted in deriving PSDM model. Additionally, it shall be assumed that homogeneity exists throughout the batch system. Accordingly, the model will be referred to as pore and surface diffusion model (PSDM). The model equations can be written as follows:

Mass Balance Inside Particle Phase

The following equation can be used for describing intra-particle mass transfer (Hand *et al.*, 1983):

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 D_s \rho_p \frac{\partial q}{\partial r}(r,t) + r^2 D_p \varepsilon_p \frac{\partial C_p}{\partial r}(r,t) \right] = \frac{\partial}{\partial t} [\rho_p q(r,t) + \varepsilon_p C_p(r,t)] \quad (2)$$

Mass Balance in Fluid-bulk Phase

The solute concentration $C(t)$ in the vessel is given by following equation (Ping and Guohua (II), 2001):

$$\frac{dC_b(t)}{dt} = -\frac{3k_f W_o}{R_p V_L \rho_p} [C(t) - C_p(r = R_p, t)] \quad (3)$$

Initial and Boundary Conditions

The initial condition for equation (2) is:

$$C_p(r, t = 0) = 0 \quad (4)$$

The initial condition for equation (3) is:

$$C_b(t) = C_o \quad (5)$$

The boundary conditions for equation (2) are:

$$\frac{\partial}{\partial r} \left[q(r,t) + \frac{\varepsilon_p}{\rho_p} C_p(r,t) \right] = 0 \quad \text{at } r = 0, t > 0 \quad (6)$$

$$D_s \rho_p \frac{\partial q(r,t)}{\partial r} + D_p \varepsilon_p \frac{\partial C_p(r,t)}{\partial r} = k_f [C(t) - C_p(r,t)] \quad \text{at } r = R_p, t > 0$$

Solving the system of partial differential equations numerically gives the unsteady state concentration of the solute in the vessel.

The bulk-fluid phase and particle phase equations for the batch adsorber model are first discretized using finite elements (FE) and orthogonal collocation (OC) method, respectively. The resulting ordinary differential equations (ODE) system is solved using an existing ODE solver provided by MATLAB V.6.5.

MATERIALS AND METHODS

Adsorbats

Phenolic compounds namely phenol and p-nitrophenol are pollutants which come to natural water resources from the effluents of a variety of chemical industries such as refineries, phenol

manufacturing, pharmaceuticals and industries of resin paint, dying, textile, petrochemical, pulp mill, etc. Consequently, aquatic organisms including fish are subjected to these pollutants. (Fleeger *et al.*, 2003).

The effect of phenolic compounds is toxic to fish, but they also impart a disagreeable taste to the fish, far below toxic limits. Therefore, even non-drinking water must be essentially free of phenolic compounds. The content of the phenolic compounds in the industrial wastewater (about 200-2000 mg/l) is usually higher than standard limit. In which the US Environmental Protection Agency (EPA) had instituted a regulation for lowering phenol content in the wastewater to less than 1.0 mg/l (Banat *et al.*, 2000), while the World Health Organization recommend a threshold permissible concentration of phenol in drinking water as 0.001mg/l (WHO,1984).

Salicylic acid is toxic in high doses. It can cause stinging, burning, skin irritation, experience dryness, peeling and flaking of the skin. Also, it is poisoning with typical preparations, symptoms of poisoning include confusion, diarrhea, nausea, vomiting, dizziness, headaches, rapid breathing, continuing ringing or buzzing in ears, severe drowsiness. (Hadier and Saifullah, 2000). The physical properties of salicylic acid ,phenol and paranitrophenol are listed in Table (1).

Adsorbent (organoclay)

The organoclay was prepared by adding hexadecyltrimethyl ammonium chloride solution (25% wt./vol. concentration and density 0.995kg/m³) with bentonite powder (calcium type, mean particle size 0.75mm) in a stainless steel container and mixed thoroughly by hand. The resulting paste was then homogenized by using meat grinder to achieve good mixing. The product (organoclay) was dried in electrical oven at 80°C for 48 hours and then ground by agate mortar followed by screening to a desirable particle size of geometric mean diameter (d_{gm}) of 0.71mm. This size was chosen because it was noted that, for sizes greater then 0.71mm particles attrition to smaller size would occur, whereas those below 0.71mm agglomerate . It appeared that 0.71mm size was a suitable choice. A specimen of the organoclay of size 0.71mm prepared at optimal ratio of amine to bentonite that gives the highest removal efficiency is shown in Figure 1.

Adsorption Isotherm Experiments

Solutions were prepared by dissolving solid solute of each type in deionized water. For all solutions prepared for this study, the pH value ranged between 6.5-6.9. A series of batch experiments were carried out to determine the adsorption isotherms of Ph,pnp and Sa from aqueous solution onto organoclay known amounts of organoclay (0.05, 0.1, 0.15, 0.2,0.5 gm) were placed in conical flasks each containing 100ml solution of concentration 0.05kg/m³ of each solute. The flasks were placed on a shaker and a agitated at room temperature for 24 hours to achieve equilibrium concentrations. Then, the solutions were filtered, and their concentrations were determined by UV-spectrophotometer (Model UV-GENESYE™ 10) at 270nm, 317nm and 295nm wave lengths for ph,pnp and Sa respectively. The adsorption capacity q_e (kg/kg) of each solute onto organoclay was calculated by the following mass balance relation:

$$q_e = \frac{V(C_o - C_e)}{W} \quad (1)$$

Where C_o and C_e are the initial and equilibrium concentration of adsorbate respectively (kg/m^3), V is the volume of solution and W is the weight of the organoclay used (kg).

Kinetic Experiments

A Two liters Pyrex beaker fitted with stainless steel mixer (400-1500rpm) (type: Heidolph RZR 2050, Electronic) was used. The beaker was filled with 1.0 liter of known concentration solution and the agitation started before adding the organoclay. At zero time, an accurate weight of organoclay (0.71mm particle size) was added. Samples of the solution were taken every 10 minutes for analysis. Each sample was returned back to the solution to keep constant volume.

During these experiments the solute concentration decreased with time, the rate of adsorption of solute was measured by monitoring the solute concentration as function of time. The desired weight of organoclay to reach related equilibrium concentration of $C/C_o = 0.05$ was calculated from the isotherm equation and mass balance equation for each solute. The desired speed was obtained by repeating the experiments for each component with different speeds (600,700,800, 900 rpm). The speed at which the concentration ratio C/C_o remains constant at 0.05 was taken as optimum speed (Jaruwong *et al.*, (2005).

The approach of $C/C_o = 0.05$ (equivalent to 95% removal efficiency) refers to the optimum operational, durability and sustainability of the adsorption process. This process will be more practical, economic wise and operational when imposing such conditions (Watts, 1998).

RESULTS AND DISCUSSION

Characterization of the Organoclay

X-Ray diffraction diagrams and total organic carbon were used to characterize natural and organoclay. As shown in Figures (2 and 3), the X-ray diffraction of the organoclay revealed a shift in peak position of $[d_{001}]$ planes (2θ changed from 6.2 to 4.78 degrees), meaning an increase in the basal spacing of these planes (Nayak and Singh, 2007). The XRD diagram Also indicating that the basal spacing of 13.6 °A for natural clay increased to 18.2 °A for modified clay. The total organic carbon is found to be (20.3%) for modified clay more larger than natural clay (1.2%). The organic carbon in the modified clay was almost entirely derived from the exchanged organic cations into the surface of clay after modification.

Adsorption Isotherms Constants

The adsorption for a single, binary and ternary component systems of (Ph, pnp and Sa) onto organoclay in batch experiments are shown in Figures 4 to 8. These experiments were conducted with initial concentrations of (0.05 kg/m^3) and particle size of (0.71mm) at room temperature in order to determine the isotherms constants for the equilibrium model tested in this work.

The constants of adsorption isotherm models for single component systems were determined using different models, while for binary and ternary component systems the combination of Langmuir-Freundlich model was used. The parameters for each model were obtained using

non-linear statistical fit of the equations to the experimental data. The parameters of different models used with correlation coefficients are summarized in Table (2).

From the figures and tables for single, binary and ternary component systems, one can conclude the following:

- The equilibrium isotherm for each solute is of favourable type (i.e somewhat convex upward) and relatively high adsorbent loading were obtained at low concentrations of solute.
- The Freundlich model gives the best fit of the experimental data for single solute systems with high correlation coefficients. The equilibrium data for binary and ternary component systems were described successfully with Langmuir-Freundlich combination model for competitive adsorption.
- The q_e values for the binary and ternary systems were less than those in single component systems due to competition between the solutes.
- The constant parameters of the Freundlich model were found to be 2.51, 2.33 and 2.27 for n and 0.314, 0.559 and 0.687 for k for ph, pnp and Sa respectively. Where k is related primarily to the capacity of the adsorbent, and n is a function of the strength of adsorption. For fixed values of C_e and n the larger the value of k , the larger the capacity (q_e). For fixed values of k and C_e , the smaller the value of n , the stronger the adsorption bond. The high value of k and the lower value of n indicated that the sorption capacity of organoclay for salicylic acid was very high compared with Ph and pnp.
- Values of molecular weight, solubility and octanol-water coefficient (Table 1) show that phenol is more hydrophilic than p-nitrophenol and salicylic acid. This is due to the adverse effect of the OH group on adsorption of phenol, which may be attributed to the capability of this group to form hydrogen bonding with water and then renders the compound less liable to be adsorbed in comparison with pnp.
- The paranitrophenol is adsorbed to greater extent in comparison with phenol itself. This is attributed to the prevention of the formation of hydrogen bond either by forming an internal hydrogen bond between OH and the substitute group or by offering steric hinderance, thereby increasing the solvophobic nature as well as sorption capacity of the solute.
- The characteristic parameters including solubility, molecular weight, natural position of the substituted group and hydrogen bonding with the solvent molecules play a decisive role in the overall adsorption process.
- The adsorption capacity can be compared for the three solutes in terms of (q_e). The maximum adsorptive capacities were 0.03, 0.0344 and 0.0358 kg/kg for ph, pnp and Sa respectively, in which the adsorptive capacity follow the sequence Sa > pnp > Ph.
- The competition between solutes in the bi-solute and tri-solute systems reduced the sorbed amount of each solute compared with that in the single-solute system.

Determination of Diffusivity Coefficients

The surface diffusion coefficient D_s and the pore diffusion coefficient D_p for ph, pnp and Sa can be determined by matching experimental concentration curves with predicted concentrations at optimum agitation speed. This can be generated by numerical solution of the batch adsorber model. The matching requires values of the following parameters:

Optimum Weight of Organoclay

This was determined from the equilibrium related concentration of ($C_e/C_o = 0.05$) using Freundlich equation with mass balance in one liter of solution as follows:

$$q_e = \frac{V_L (C_o - C_e)}{W_o} = KC_e^{1/n} \quad \text{Where} \quad W_o = \frac{V_L (C_o - C_e)}{KC_e^{1/n}} \quad (7)$$

The optimum weights of organoclay for Ph, pnp and Sa were found to be 1.67×10^{-3} , 1.12×10^{-3} and 0.967×10^{-3} kg respectively.

Optimum Agitation Speed

The concentration-decay curves of solutes are shown in Figures (9, 10 and 11) for Ph, pnp and Sa respectively at different agitation speeds (600, 700, 800, 900 rpm). The effluent concentration equal to 5% of inlet concentration was taken as the breakthrough point. The optimum agitation speed needed to achieve $C_e/C_o = 0.05$ was found to be 800 rpm. It is seen from the graphs that if the speed exceeds 800 rpm, the equilibrium relative concentration is less than 0.05, with possible attrition of the organoclay and consequently ending with powdered rather than granular organoclay.

External Mass Transfer Coefficient in Batch Adsorption (k_f)

The external mass transfer coefficient (k_f) was determined from the concentration decay curves at optimum agitation speed at the initial rate data, using the following equation (Alexandar and Zayas, 1989):

$$k_f = -\frac{R_p \rho_p V_L}{3W_o t} \ln \left(\frac{C_t}{C_o} \right) \quad (8)$$

Where, C_o and C_t are the solute concentration at time zero and time t respectively. For accurate estimation of K_f , samples were taken after 2, 4 and 6 minutes and analyzed immediately. Generally, at $R_p = 0.35$ mm, $\rho_p = 1025$ kg/m³, $V_L = 1 \times 10^{-3}$ m³ and at the given amount of organoclay for each solute the average calculated values of K_f were found to be 0.61×10^{-4} , 1.32×10^{-4} and 1.96×10^{-4} m/s for Ph, pnp and Sa respectively.

The pore and surface diffusion coefficients were obtained by matching experimental and predicted data from mathematical model. As shown in Figures 12 to 14. The results are as follows:

- Ph: $D_p = 0.13 \times 10^{-14} \text{ m}^2/\text{s}$, $D_s = 0.18 \times 10^{-10} \text{ m}^2/\text{s}$, $R^2 = 0.9965$
- pnp: $D_p = 0.41 \times 10^{-14} \text{ m}^2/\text{s}$, $D_s = 0.35 \times 10^{-10} \text{ m}^2/\text{s}$, $R^2 = 0.991$
- Sa: $D_p = 0.85 \times 10^{-14} \text{ m}^2/\text{s}$, $D_s = 0.62 \times 10^{-10} \text{ m}^2/\text{s}$, $R^2 = 0.9921$.

Examining the results shown above it can be seen that:

- the rate of mass transfer of Sa is higher than the Ph and pnp and Sa has the largest value of D_s and D_p in comparison with Ph and pnp. This indicates that Sa is being adsorbed at faster rate than others. The results also indicate that the surface diffusion was controlling the adsorption process.
- There is good matching between experimental and predicted data in batch experiments using pore-surface diffusion model for each solute.

CONCLUSIONS

- Modification of natural clay to organoclay is resulting through the exchange of quaternary amine (hexadecyltrimethyl ammonium HDTMA⁺) cation in place of Ca⁺ at the surface of bentonite . From XRD diagrams it is seen that the basal spacing of 13.6 °Å for natural clay increased to 18.2 °Å for modified clay. After modification the total organic carbon increased from 1.2% to 20.3% for natural and modified clay respectively.
- There is a good matching between experimental and predicted data using pore-surface diffusion model for all solutes. Hence, the transfer of solutes within the organoclay is controlled by surface diffusion.
- The adsorption capacity for binary systems onto organoclay are found to follow the sequence

$$\text{pnp} > \text{Ph} , \text{Sa} > \text{Ph} , \text{Sa} > \text{pnp}$$

whereas the sequence for ternary system is as follows:

$$\text{Sa} > \text{pnp} > \text{Ph}$$

- The competition between solutes in binary and ternary sorption systems caused reduction in the sorbed amount of each solute compared with that in single solute system.
- the lower adsorption capacity of Ph may be explained by its higher solubility, low molecular weight and low octanol-water coefficient compared with pnp and Sa, and vice versa with the Sa.

Acknowledgements

The authors are very great thankful to the staff of the environmental and Chemical engineering departments at the university of Baghdad for their continual support throughout the research.

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