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Kinetics of p-Nitrophenol adsorption from water by using montmorillonite clay

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Abstract
Montmorillonite clay is used to remove p-nitrophenol (PNP) from aqueous solution. Effect of contact time on the removal efficiency of PNP by montmorillonite clay is investigated the kinetics of the PNP removal by montmorillonite clay is in well agreement with the pseudo first order model. The mass transfer behaviour is due to the pore blockage and steric repulsive behaviour induce by adsorbed PNP on the mont morillonite surface.

Keywords: PNP, Montmorillonite clay, pseudo first order model, diffusion, adsorption

Introduction
The phenols and their derivatives especially p-nitro phenol are the most pollutants of natural water. Montmorollinite clay is used as adsorbment for wastewater treatment. Kinetics investigations of the montmorillonite clay are under taken in the present study.
Pseudo first order and pseudo second order kinetics models are usually adopted in kinetics investigations. The pseudo first order equation is a simple kinetics process of liquid- Solid phase adsorption. It was forwarded by Lagergress (1898). It's non linear formula is given as follows

$$Q_T = Q_E (1-e^{-k1t})$$

Where k_1 is the rate constant of the pseudo first order adsorption
(min^{-1}). Obviously, Q_E and K_1 can be figured out by plotting Q_T verses t by further non linear regression analysis. The pseudo second order model based on the adsorption equilibrium capacity may be expressed as the following linear form (HO and Mckay 1999).

$$T/Q_T = T/Q_E + 1/k_2(Q_E)^2$$

Where k_2 is the rate constant of pseudo second order adsorption [g/mg.min]. Obviously Q_E and k_2 can be determined experimentally by plotting T/Q_T versues T.

Materials and Methods
The montmorillonite clay is used in the present work. It was powdered to particles of size less than 50 micro metre. montmorillonite clay was prepared by washing several times with distilled water to clean the soluble.

Chemicals: PNP, HCl, NaOH, Na_2SO_4, $NaHCO_3$, Na_2HPO_4, NaCl etc.

Characterisation Techniques
X-Ray diffraction (XRD) patterns were conducted using a siemens D5000 diffractometer using Cu -kalpha radiation (Cu- K alpha =1.5418 A) with the scanning step of 0.04 degree speed of XRD analysis of 5s/ste. Fourier transform infrared (FTIR) spectra were measured using a thermo scientific Nicolet iS10 spectrometer with the resolution of 4 cm^{-1}, in the range of 400=4000 cm^{-1}.

Adsorption Experiments

Adsorption tests were conducted using both system. A certain amount of adsorbent was included into 50 ml of PNP solution at desired concentrations. The removal efficiency and adsorption capacity at equilibirium were calculated as follows :

$$\% \text{ removal} = (C_0 - C_E)*100 / C_0$$
$$q \text{ (mg/g)} = (C_0 - C_E)*V / m$$

where C_0 and C_E are initial and equilibirium concentrations of BNP in mg/l respectievely. m(g) is the amount of adsorbent and V (l) is the volumne of solution.

Results and Discussion

Characterisation of the Adsorbent

The phase and crystallinity of montmorillonite clay were determined by XRD measurement (fig 1)

At 2 theta =6.68 degree, the based spacing (d_{001}) is 1.32 nm.The diffraction peaks at 2 theta =19.61, 27.92, 35.09 and 60.2 were corresponding to the main mineral component of montmorollinite (standkovicetal. 2011) fig 1

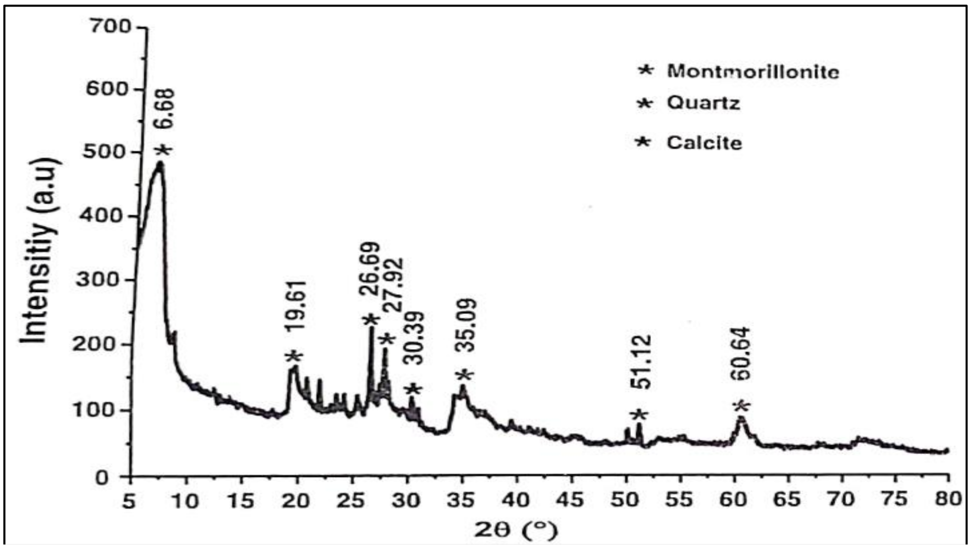

Fig 1: Powder X – Ray diffraction of montmorillonite clay

Effect of Contact Time

The effect of contact time on the PNP removal by montmorillonite clay was investigated in the time range 0-240 min to determine the equilibirium time of adsorption. The results are illustrated in fig 2

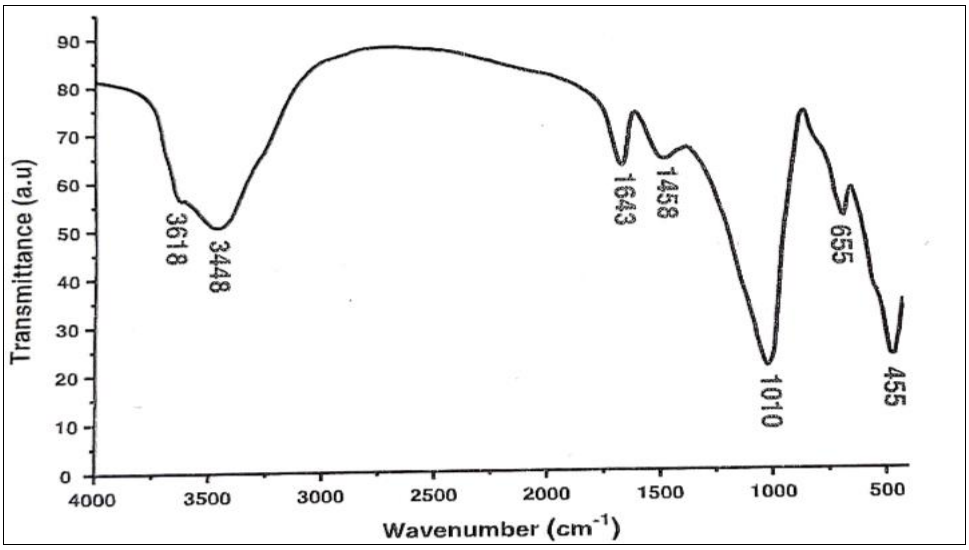

Fig 2: FT-IR spectra of montmorillonite clay in the range of 400-4000 cm^{-2}

Adsorption Kinetics

The experimental kinetic data of PNP adsorption on the montmorillonite clay were analysed by pseudo first order and pseudo second order model.

The non linear regression analysis of kinetic data is represented in fig 3.Kinetic parameters are tabulated in table 1. q_e (mg/g) and q_t (mg/g) are respectievely adsorbed amounts of PNP at equilibirium and time t(min) k_1 (min^{-1}) and K_2 (g/mg.min) are first order and 2^{nd} order rate – constants respectievely. Based on the results and comparing the R^2 factor the kinetics of the PNP removal by montmorillonite clay is agreement with pseudo first order model.

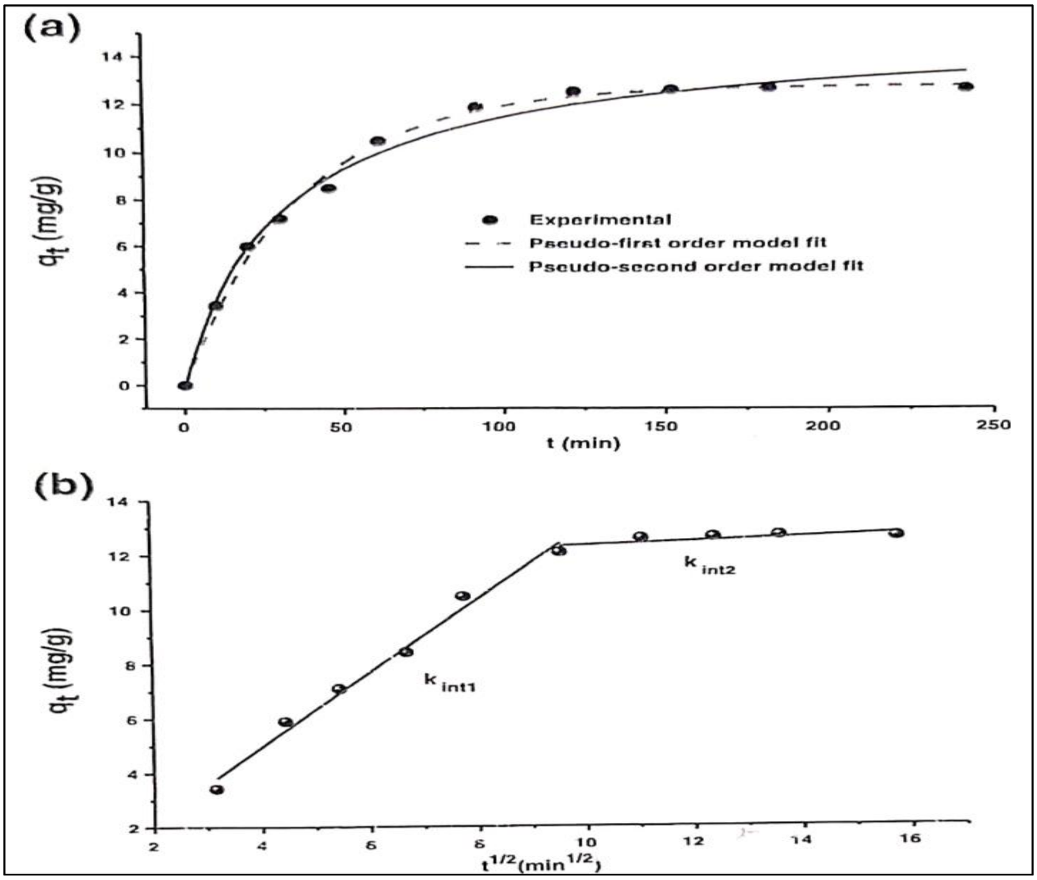

Fig 3: (a) pseudo firdst order (b) pseudo 2nd order.

Table 1: Kinetic model parameters for PNP adsorption on the montmorollonite clay

Kinetic models	Equations	Parameters	
Pseudo-first-order	$q_t = q_e(1-e^{-k_1 t})$	$q_{e.1}$ (mg/g)	12.99
		k_1 (min^{-1})	0.028
		R^2	0.995
Pseudo-second-order	$q_t = \frac{q_e^2 k_2 t}{1+q_e k_2 t}$	$q_{e.1}$ (mg/g)	15.39
		k_2 (g/mg min)	0.002
		R^2	0.988
Intraparticle diffusion	$q_t = k_{int} t^{1/2} + C$	k_{int1} (mg/g min$^{1/2}$)	1.380
		k_{int2} (mg/g min$^{1/2}$)	0.093

Conclusion
The removal of PNP by montmorollonite clay from aqueous solutions was carried out in a batch system. PNP adsorption on the montmorollonite clay were analysed by the pseudo first order and pseudo second order models.the mass transfer behaviour may be due to the pore blockage and steric repulsive barrier induced by adsorbed PNP on the montmorollonite clay surface.

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