

Equilibrium, Kinetic and thermodynamic studies on phenol sorption to clay

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Abstract

The sorption efficiency of low cost sorbent clay in removing phenol and m-nitrophenol (MNP) from aqueous solutions has been investigated in batch experiments. The effects of particle size of sorbent, pH, phenol concentration and temperature have been studied. The sorption isotherm has been studied in terms of the Langmuir model. The experimental data were well fitted by the Pseudo second-order kinetic model allowing the rate constant to be evaluated. This study showed that clay could be used as an efficient sorbent material for the sorption of phenols from aqueous solutions. This study is important for treatment of phenolic effluents where continuous removal can be achieved on a large scale.

Keywords: Sorption, Pseudo second order equation, m-nitrophenol, Clay, Efficient sorbent.

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Introduction

Phenol and its derivatives are the priority pollutants since they are toxic and harmful to organisms even at low concentration.¹ Beside their toxic effects, phenolic compounds create an oxygen demand in receiving waters and impart taste and odour to water with minute concentration of their chlorinated compounds. Surface and ground waters are contaminated by phenolics as a result of the continuous release of the compounds from petrochemical, coal conversion and phenol producing industries. In addition to these industries, olive oil production is another source for the release of phenol due to the high phenol content of olive mill effluents.² Many phenols have been classified as hazardous pollutants because of their potential toxicity to human health.³ Like chlorophenols, nitrophenols (NPs) are among serious environmental contaminants. As secondary pollutants arising from aromatic hydrocarbon and nitrogen oxide emissions by photochemical reactions in the atmosphere, NPs have been identified in cloud, fog water condensates as well as on airborne particulate matter⁴ and are sources of surface water, ground water and soil pollution.

Furthermore, phenolic pollutants are transferred to soils from industrial productions and from the use of pesticides. The latter are responsible for the occurrences of 2-nitrophenol, 4-nitrophenol, 4, 6-dinitro-o-cresol and 2, 4-dinitro-6-sec.butylphenol in the environment. The Ministry of Environment and Forests (MOEF), Government of India and EPA, USA, have listed phenol and phenolic compounds on the priority – pollutants list⁵. The permissible limits⁶ for phenolic concentrations in industrial effluents before discharging into municipal sewers and surface waters are 5.0 and 1.0 mgdm⁻³. Nitrophenols are bioplasmic poisonous compounds. Their toxicity lies in the chemical reaction with protein in the bioplasm of organism cell, producing insoluble protein and resulting in the loss of activity of the cell.⁷

Environmental problems which are associated with the presence of phenols in natural waters have resulted in developing the methods for the removal of phenol⁸. Several methods for the treatment of phenolic wastewater have been proposed in the literature. These include physicochemical treatment processes, chemical oxidation and biological degradation. The physicochemical processes include adsorption and ion exchange. Some of the adsorbents used in the removal of phenols include sawdust, flyash, peat and bentonite.^{9,10} Earlier workers have prepared high quality activated carbons from

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biomass/plant materials for treating wastewater containing phenols.^{11,12} Given the strict environmental authorities guidelines regulating the discharge of organic compounds to the environment, it is important to develop attenuating materials capable of adsorbing these types of compounds. While there are many compound groups present as contaminants in the geo-environment, this paper has focused on ‘phenolics’.¹³ The present paper deals with the study of the feasibility of removal of phenol by clay under equilibrium and kinetic conditions in an endeavor to use the data for the design of an economical and flexible batch reactor system of phenol removal.

Materials and Methods

Adsorbent

The clay was obtained from the mines of Katni district (Madhya Pradesh), India. The clay was sieved through standard test sieves into different particle sizes 140, 100, and 50 μ m and dried for 2 hours at 110^o C in an electric oven and stored in a dessicator for use. The analysis of clay has been carried out by chemical methods¹⁴ and its composition is given in Table 1.

Table 1. Chemical analysis of a fraction of clay.

Chemical composition	Weight (%)
SiO ₂	48.12
Al ₂ O ₃	34.54
Fe ₂ O ₃	2.48
CaO	0.83
MgO	0.50
TiO ₂	0.40
LOI (800 ^o C)	12.44
specific gravity	2.10 g cm ⁻³
surface area	1.15 m ² g ⁻¹
porosity	0.23

Adsorbates

Two organic molecules were selected for the study of adsorption onto clay: phenol and m-nitrophenol. The adsorbates, purchased from Sigma with purity greater than 99.5% were used to prepare the aqueous solutions for the adsorption tests. The principal characteristics of the studied adsorbates are regrouped in Table 2.

Batch isotherm and kinetic

The sorption isotherm study was performed by batch sorption experiments. A series of 100ml of stoppered

flasks were employed, each having 50 ml of aqueous phenolic solutions of various concentrations. The sorbent (200 mg) of sorbent was then added into each flask and agitated for 2 hrs. The pH of the solution was adjusted with HCl or NaOH solution by using a pH meter. Temperature controlled shaking thermostat was used to control the desired temperature. The effect of experimental parameters such as different particle size of clay (50 μ m, 100 μ m, 140 μ m), pH value (2.0, 4.0, 6.5, 8.0, 10.0) and temperature (30, 40, 50^o C) were studied. A constant speed of 65-70 rpm was maintained for each run throughout the experiment to ensure uniform mixing. The stirring rate was kept quite low (65-70 rpm) in order to reproduce in the laboratory a condition similar to the one present in the natural water system. Blanks were run simultaneously without any sorbent. After attainment of equilibrium, the sorbent was removed by centrifugation at 10,000 rpm and the progress of sorption was determined spectrophotometrically (Systronic Digital Spectrophotometer 166), using 4- aminoantipyrine at λ_{max} = 500 nm which corresponds to maximum absorbance. The concentrations of the residual phenol, C_e were determined by Standard Methods.¹⁵ The percentage of adsorbed phenol on clay was calculated by the difference obtained between the initial and final concentrations of the solution.

In the experiments of Batch kinetic sorption, 35 ml of the chosen desired concentrations of phenols solution were placed in a 100 ml conical glass stoppered flasks with 200mg of clay and placed in a thermostatic shaker at various particle size (50 μ m, 100 μ m, 140 μ m), pH values (2.0, 4.0, 6.5, 8.0, 10.0), concentrations (500, 300, 200 mg L⁻¹), and temperatures (30, 40, 50^o C). At predecided intervals of time, samples were taken, and their concentrations were determined.

Table 2. Characteristics of adsorbates.

Characteristics	Phenol	m-Nitrophenol
Molecular wt (g mol ⁻¹)	94	139
pK _a (ref 34)	9.9	8.1
Solubility (g L ⁻¹)	93 (ref 35)	14 (ref 36)

Results and Discussion

Sorption equilibrium isotherms

The sorption data were analysed using Langmuir isotherm model.¹⁶ The equilibrium data for the sorption of phenols on clay at different particle sizes, temperatures and pH value follows the rearranged Langmuir equation.

Langmuir isotherm has found successful application in many real sorption processes. The Langmuir isotherm equation can be written as follows:¹⁷

$$q_e = \frac{Q_0 b C_e}{(1 + b C_e)} \quad (1)$$

The above linearized Langmuir equation is represented as follows:¹⁸

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (2)$$

Where C_e is equilibrium concentration of the phenol (mg L^{-1}), q_e is the amount sorbed at equilibrium (mg g^{-1}). The constant Q_0 signifies the sorption capacity (mg g^{-1}), and b is related to the energy of adsorption (L mg^{-1}). The plots of C_e/q_e vs C_e at different conditions were found to be linear indicating the applicability of the Langmuir model. The statistical significance of the correlation coefficient (R^2) for C_e/q_e vs C_e was the criteria by which the fitting of the data to Langmuir isotherm was tested. The parameters Q_0 and b have been calculated and the results are represented in Tables 3- 5.

Adsorption kinetics

The kinetics of phenol sorption on clay was treated using the pseudo second order model. To investigate the mechanism of sorption, the constants of sorption were determined by using a pseudo second – order mechanism. The pseudo second order rate expression may be written as¹⁹:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \quad (3)$$

Equation (2) can be rearranged to a linear form:

$$\frac{t}{q_t} = \frac{1}{k q_e^2} + \frac{1}{q_e} t \quad (4)$$

$$h = k q_e^2 \quad (5)$$

Where q_t (mg g^{-1}) is the amount of phenol sorbed at time t , q_e (mg g^{-1}) is the amount sorbed at equilibrium, k is Pseudo-second order rate constant ($\text{g mg}^{-1} \cdot \text{min}^{-1}$) and h is the initial sorption rate. The values of k were determined from the slope of the plots t/q_t vs time for phenols under different conditions and thus are given in Tables 3-6. The correlation coefficients (R^2) for the linear plots are superior

to 0.99 in all the systems and so sorption system can be considered as a Pseudo-second order model.

Table 3. Sorption isotherm and kinetic parameters for different fractions of clay.

Sorbate	Particle Size of Sorbent (μm)	Langmuir Parameters			Rate constant	
		Q_0 (mg g^{-1})	b (L mg^{-1})	R^2	k ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
Phenol	50	34.349	0.0348	0.9998	4.21×10^{-3}	0.9998
	100	30.959	0.0314	0.9998	3.93×10^{-3}	0.9998
	140	27.842	0.0310	0.9991	3.40×10^{-3}	0.9998
m-nitrophenol	50	48.415	0.0431	0.9994	4.96×10^{-3}	0.9999
	100	44.833	0.0395	0.9996	4.83×10^{-3}	0.9999
	140	41.568	0.0374	0.9997	4.66×10^{-3}	0.9999

Sorption Isotherm Conditions: pH 6.5 and Temperature 30°C; Kinetic Conditions: pH 6.5; Temperature 30°C and Concentration 500 mg L^{-1} .

Table 4. Sorption isotherm and kinetic parameters for different pH values.

Sorbate	pH values	Langmuir Parameters			Rate constant	
		Q_0 (mg g^{-1})	b (L mg^{-1})	R^2	k ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
Phenol	2.0	40.121	0.0370	0.9998	4.49×10^{-3}	0.9998
	4.0	36.818	0.0363	0.9996	4.45×10^{-3}	0.9998
	6.5	34.349	0.0348	0.9998	4.21×10^{-3}	0.9998
	8.0	31.925	0.0294	0.9989	4.05×10^{-3}	0.9999
	10.0	29.0455	0.0265	0.998	3.80×10^{-3}	0.9999
m-nitrophenol	2.0	52.579	0.0456	0.9995	5.70×10^{-3}	0.9999
	4.0	50.395	0.0446	0.9995	5.21×10^{-3}	0.9999
	6.5	48.415	0.0431	0.9995	4.96×10^{-3}	0.9999
	8.0	45.855	0.0388	0.9998	4.87×10^{-3}	0.9999
	10.0	43.424	0.0376	0.9996	4.72×10^{-3}	0.9999

Sorption Isotherm Conditions: Size 50 μm and Temperature 30°C; Kinetic Conditions: Size 50 μm ; Temperature 30°C and Concentration 500 mg L^{-1} .

Table 5a. Sorption isotherm and kinetic parameters for different temperatures.

Sorbate	Temperatures ($^{\circ}\text{C}$)	Langmuir Parameters			Rate constant	
		Q_0 (mg g^{-1})	b (L mg^{-1})	R^2	k ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
Phenol	30 \pm 1	34.348	0.0348	0.9998	4.21×10^{-3}	0.9998
	40 \pm 1	37.209	0.0365	0.9997	4.66×10^{-3}	0.9998
	50 \pm 1	40.105	0.0378	0.9994	4.87×10^{-3}	0.9998
m-nitrophenol	30 \pm 1	48.415	0.0431	0.9994	4.96×10^{-3}	0.9999
	40 \pm 1	51.983	0.0444	0.9995	5.22×10^{-3}	0.9999
	50 \pm 1	55.854	0.0451	0.9998	5.42×10^{-3}	0.9999

Sorption Isotherm Conditions: pH 6.5 and Size 50 μm ; Kinetic Conditions: pH 6.5; Size 50 μm and Concentration 500 mg L^{-1} .

Table 5b. Thermodynamic parameters at different temperatures.

Sorbates	Temperature ($^{\circ}\text{C}$)	K	Thermodynamic Parameters		
			ΔG° (kcal mol^{-1})	ΔS° (cal mol^{-1})	ΔH° (kcal mol^{-1})
Phenol	30	1.1953	-0.1074	8.296	2.4065
	40	1.3581	-0.1904	4.1364	1.1043
	50	1.5159	-0.2670	-	-
m-nitrophenol	30	2.0867	-0.4429	7.732	1.8999
	40	2.3080	-0.5202	4.4687	0.8785
	50	2.5190	-0.5929	-	-

Conditions: pH 6.5 and Size 150 μm .

Effect of particle size

It is clear that decrease in sorbent particle size from 140µm to 50µm the sorption of different ions increases because the sorption capacity is directly proportional to the total exposed surface and inversely proportional to particle diameter for a non-porous sorbent such as clay and are shown in Figures 1 and 4. This is due to the fact that sorption being a surface phenomenon; the smaller sorbent sizes offered comparatively larger surface area and hence higher phenol removal at equilibrium²⁰. The relationship between the effective surface area of the sorbent particles and their sizes is that the effective surface area increases as the particle size decreases and as a consequence, the sorption capacity per unit mass of the sorbent increased²¹.

So the smaller clay particle sizes for a given mass of clay have more surface area and therefore the number of available sites is more. This can be explained by the fact that for smaller particles large external surface area is presented to the phenol molecules in the solution which results in a lower driving force per unit surface area for mass transfer than when larger particles used.

The sorption capacity increases by the introduction of a nitro group (-NO₂) into the benzene ring which increases the acid character (conjugation effect) responsible for forming an anion on the oxygen atom of the -OH group and which has a strong affinity for alumina and silica surfaces. It is also clear that for nitro phenol both functional groups may be separately or simultaneously involved in the sorption process. Other authors have also

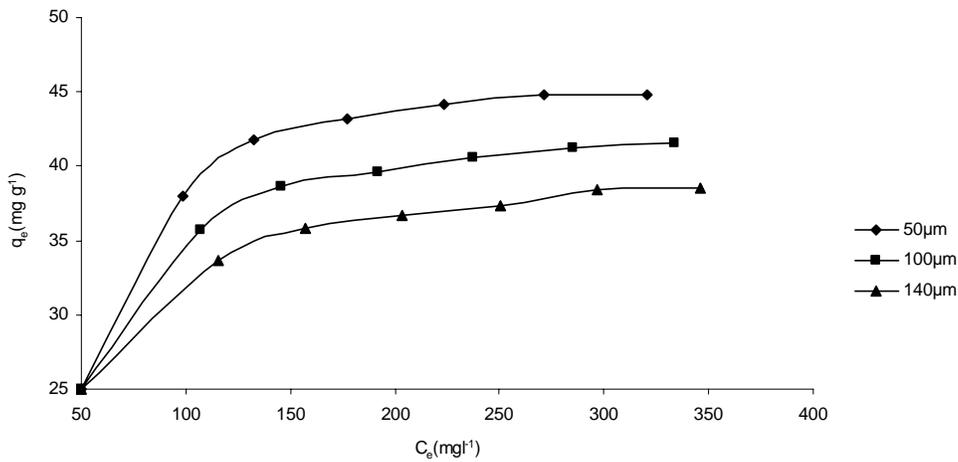


Fig 1-Sorption isotherms for m-nitrophenol on clay ; pH 6.5, Temperature 30°C

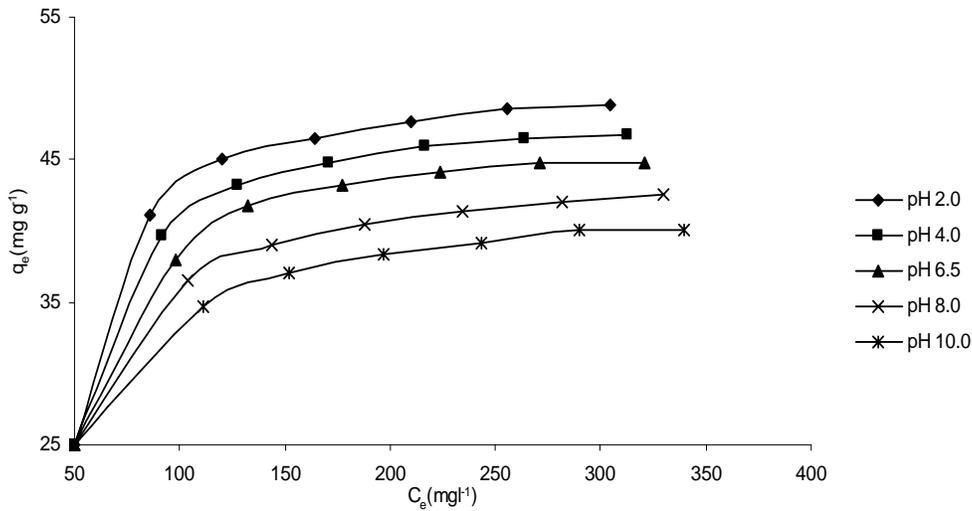


Fig 2-Sorption isotherms for m-nitrophenol on clay ; size 50µm, Temperature 30°C

Effect of pH

The removal of pollutants from waste and wastewater is affected significantly by the pH of the medium from which the removal occurs. The percentage of adsorption decreases as the pH increases as shown in Figures 2 and 5. The experimental data show that the percentage of clay removed at pH 2 is 36.32 and it has been observed that the same decreases with increase in pH. For example, at pH 6.5 the percentage of clay removed is 31.46, while at pH 8 it is about 29.46 and at pH 10 the clay removed is 28.64 percent. The influence of pH on the pronounced sorption of phenol on the surface of the material at low pH ranges leads to the assumption that chemisorption dominates in this range and chemisorption along with physisorption occurs at higher pH ranges²³. The reason may be attributed to the large number of H⁺ ions present at low pH

values which in turn neutralized the negatively charge adsorbent surface. This may be explained on the basis of formation of a positively charged surface in an acid medium and a negatively charged oxide surface in basic medium from hydroxylated oxide surface to clay²⁴.

This can be explained by the differences in the solubility. The solubility seems play a very significant role in adsorption. A decrease in solubility and pK_a is associated to an increase in adsorption capacity. As the NO₂ group is introduction to the phenol resulted increased sorption due to decreased water solubility. An inverse relationship exists between sorbate solubility and its sorption potential. Low solubility implies that weak forces exist between solvent and sorbate molecules as a result; high amount of uptake took place. A nitro group in phenol lowers the electron density in the ring in comparison with phenol. Similar results were found by other workers²⁵.

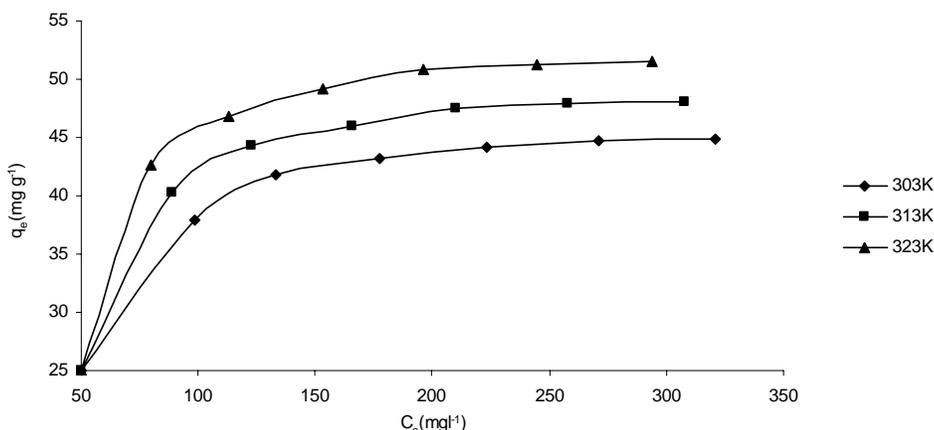


Fig 3 -Sorption isotherms for m-nitrophenol on clay ;size 50µm; pH 6.5.

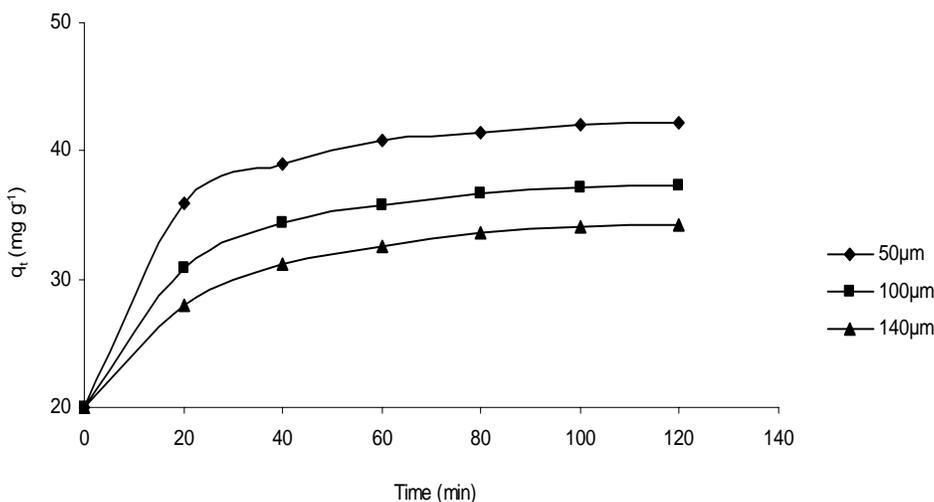


Fig 4- Sorption Kinetics of m-nitrophenol on Clay .Concentration 500 mg l⁻¹; pH 6.5; Temperature 30°C.

Effect of temperature and thermodynamic parameters

In order to understand the effect of temperature on the adsorption of phenols, experiments were also conducted at different temperature. The percentage of adsorption of phenol increases by increasing temperature indicating the process to be endothermic as shown in Figures 3 and 6. The effect of temperature can be explained on the basis of hydrogen bonding. In aqueous solutions of phenols, there exist extensive hydrogen bonding between the phenol molecule and water, resulting in appreciable solubility. The hydrogen bonds get broken at higher temperatures and, this would cause phenol to be less soluble and, therefore, exhibit a higher tendency to go to the adsorbent surface and adsorbed rather remaining in solution²⁶. The sorption capacity also increases suggesting that the active surface centers available with sorption have increased with temperature²⁷. Similar results were also obtained by other workers²⁸.

The standard free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) were calculated using the following equation²⁹

$$\Delta G^0 = - RT \ln (K) \quad (6)$$

$$\Delta H^0 = R \frac{(T_1 T_2)}{(T_2 - T_1)} \ln \frac{K_2}{K_1} \quad (7)$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (8)$$

Where K is equilibrium constant for the adsorption process, which can be expressed as the product of the Langmuir constants Q_0 and b ³⁰. K , K_1 and K_2 are equilibrium constant at temperature T , T_1 and T_2 respectively and R is the gas constant. The thermodynamic parameters are presented in Table 6. Positive values of ΔH^0 suggest the endothermic nature of the sorption and the negative values of ΔG^0 indicate the spontaneous nature of the sorption process. However, the values of ΔG^0 decreased with an increase in temperature, indicating that the spontaneous nature of adsorption is inversely proportional to the temperature. The positive value of ΔS^0 shows the increased randomness of the solid/solution interface during the sorption of phenol on clay. The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational energy than the energy lost by the adsorbate ions, thus allowing the prevalence of randomness in the system. The enhancement of adsorption at higher temperatures may be attributed to

the enlargement of pore size and / or activation of the adsorbent surface¹³.

Table 6. Sorption Kinetic Parameter at different concentrations.

Sorbate	Concentration (mg L ⁻¹)	Rate constant	
		k (g mg ⁻¹ min ⁻¹)	R ²
Phenol	200	5.19×10 ⁻³	0.9996
	300	4.77×10 ⁻³	0.9998
	500	4.21×10 ⁻³	0.9998
m-nitrophenol	200	5.88×10 ⁻³	0.9999
	300	5.62×10 ⁻³	0.9999
	500	4.96×10 ⁻³	0.9999

Conditions: Size 50 μm, pH 6.5 and Temperature 30°C.

Effect of concentration

The percentage of adsorption of phenol decreases as the concentration increases (Figure 7). But the rate of sorption and amount sorbed both increases with increasing concentration. Thus rate of removal of phenol is observed to increase as the concentration of these sorbate increases. This is in agreement with the findings that the rate of uptake of sorbate is found to increase non-linearly with increasing concentration of solute³¹. Moreover, in agreement with the statement that 'the removal rate related to initial concentration is more rapid the more dilute the solution', a greater fraction of the solute originally present will be adsorbed in a given period of time. Similar results were found by various authors³².

However, the sorption rate constant, k , determined using the Pseudo-second order rate order equation, varies in the reverse manner because at high concentrations the fractional adsorption is low³³. So the reverse variation in k is probably a result of a lower fractional sorption value (low percentage sorption) at higher concentrations. Thus the k values vary in the reverse order.

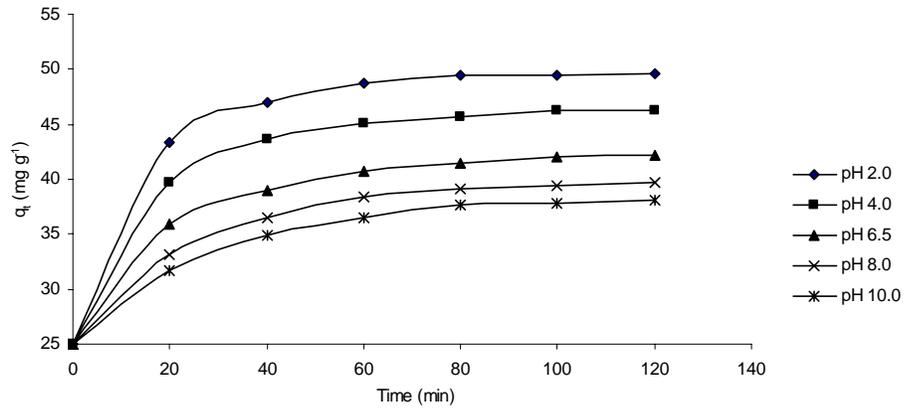


Fig 5-Sorption Kinetics of m-nitrophenol on Clay .Concentration 500mg l⁻¹; Size 50µm; Temperature 30°C.

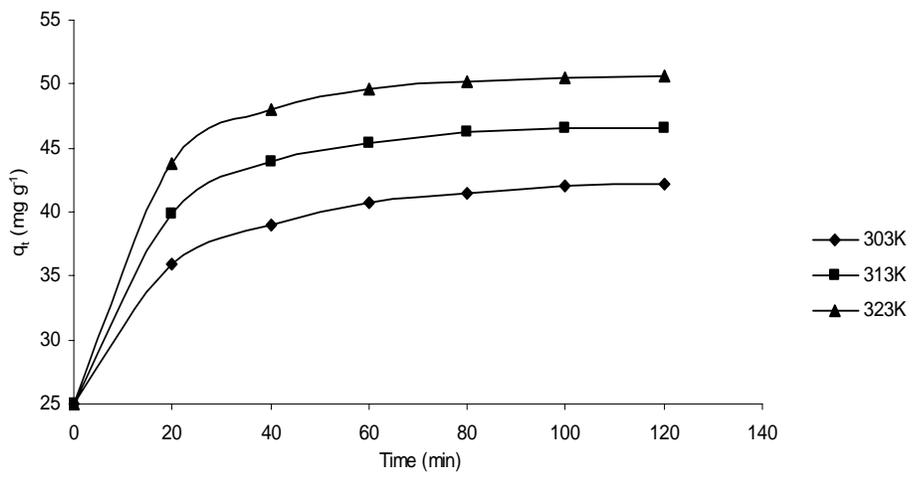


Fig 6-Sorption Kinetics of m-nitrophenol on Clay. Concentration 500 mg l⁻¹; pH 6.5; Size 50µm .

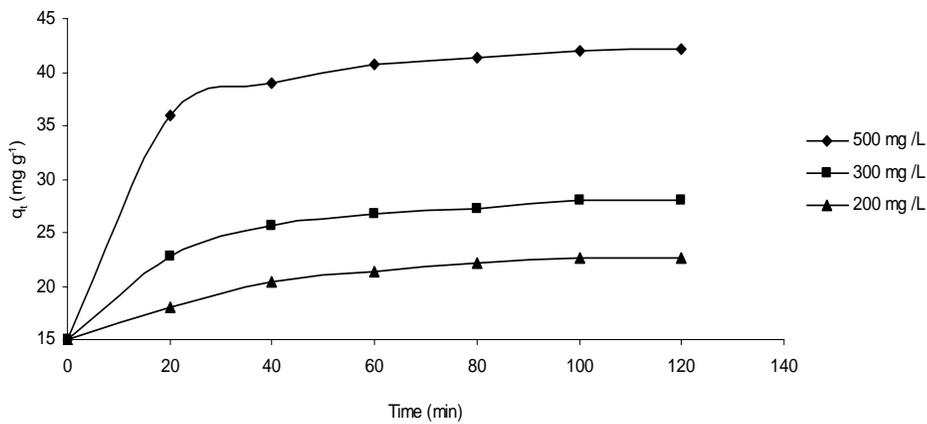


Fig 7-Sorption Kinetics of m-nitrophenol on Clay. Size 50µm;pH 6.5; Temperature 30°C.

Conclusions

1. The present study revealed that under appropriate conditions the sorption technique may be satisfactorily used for the removal of phenol and m-nitrophenol by clay.
2. In search of cheap sorbents for waste water treatment, the studied carried out on easily available mineral clay.
3. This study is important for designing batch reactor for treatment plant for phenolic effluents where continuous removal can be achieved on a large scale.
4. The percentage removal of phenol ($50\mu\text{m} > 100\mu\text{m} > 140\mu\text{m}$) and the sorption parameters for phenols Q_0 , b , k (MNP) $> Q_0$, b , k (Phenol) varies as follows for different particle size.
5. The percentage removal of phenol ($\text{pH } 2.0 > \text{pH } 4.0 > \text{pH } 6.5 > \text{pH } 8.0 > \text{pH } 10.0$) and the sorption parameters for phenols Q_0 , b , k (MNP) $> Q_0$, b , k (Phenol) varies as follows for different pH.
6. The percentage removal of phenol ($50^\circ\text{C} > 40^\circ\text{C} > 30^\circ\text{C}$) and the sorption parameters for phenols Q_0 , b , k (MNP) $> Q_0$, b , k (Phenol) varies as follows at different temperature.
7. The percentage removal of phenol ($500 \text{ mg L}^{-1} > 300 \text{ mg L}^{-1} > 200 \text{ mg L}^{-1}$) and rate constant for phenols k (MNP) $> k$ (Phenol) varies as follows for different concentration

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