Potential removal of phenol using modified laterite adsorbent

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Phenol is a notorious persistent bioaccumulative toxic substance. Being a primary pollutant, phenol has to be removed completely due to its toxicity even at low concentrations. Now-a-days the use of low cost adsorbents for the effective removal of contaminants from waste water poses a big challenge to the researchers. Modified laterite, a cheap and effective adsorbent was chosen as the adsorbent in the present study. The experiments were carried out to identify optimum values of different parameters that influence the process such as contact time, pH, initial concentration and adsorbent dosage *etc*. The kinetics of the adsorption process were also studied and found that pseudo second order model was the good fit. Three different isotherm models, *viz*., Langmuir, Freundlich and Temkin were applied and observed that Freundlich model was obeyed with good agreement. The investigation shows that modified laterite as a low cost adsorbent, can efficiently remove phenol from waste water.

Keywords: Adsorption, Isotherm models, Kinetics, Phenol, Toxicity, Waste waters

In recent years, removal of phenol and phenolic compounds from waste waters has become a burning issue because many countries made it mandatory to remove these compounds before disposal of waste water. The presence of phenols in water gives rise to unpleasant odour and being toxic the aquatic life gets highly affected. Being a bioaccumulative toxic substance, the presence of phenol in drinking water affects the functioning of liver and kidneys in human beings. Ramesh *et al*.[1] attributed the presence of phenols in excessive quantities in drinking waters as the main cause behind Uddanam endemic nephropathy[1]. The studies of Prasanna Kumari and Jagannadham[2-5] revealed that the physicochemical interactions of protein and phenol leading to structural changes of several proteins would act adversely on animal and human health. According to World Health Organization, the permissible concentration of phenolic compounds in industrial effluents is 0.5 mg/L and in drinking water as 0.002 mg/L. Among numerous techniques available, in the present day, adsorption has emerged as one of the best methods because it is simple and effective[6,7]. Although many adsorbents including natural materials[8], biosorbents[9,10] and waste

materials from industries[11] and agriculture[12] were used for removal of phenolic compounds from water, still there is a need for examining a very cheap and abundantly available adsorbent. In this regard the present investigation is aimed at inspecting the suitability of modified laterite as an adsorbent[13-15]. The present investigation is envisaged to study the effects of different parameters such as contact time, pH, initial concentration and adsorbent dosage *etc*. on adsorption of phenol; and to examine the adsorption process as per the well established isotherms; and also to inspect the kinetics of the adsorption process.

Materials and Methods

Natural laterite which was used in the present study was procured from Technoquips Separation Pvt. Ltd., Paschim Midnapur district, West Bengal, India. The natural laterite was crushed and sieved to obtain the particle size −32+60 Tyler sieves so that the mean size of the particles is 0.375 mm. This fraction was used to improve the characteristics of laterite as an adsorbent (modified laterite). Methodology adopted by the authors to prepare the modified laterite was suggested by Chatterjee and De[16].

To prepare the stock solution, the necessary quantity of phenol was dissolved in triple distilled water from which solutions of required concentrations

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of the phenol were prepared by dilution as needed further experimentation.

Batch experiments were conducted by taking 100 mL of phenol solution of specified concentration with one gram of modified laterite in stoppered conical flasks with continuous shaking. The same procedure was repeated for different batches by changing the operating parameters. Experimentation for each batch was repeated for three times and average values were considered for further calculations. Samples collected from the experiments were centrifuged, filtered and analyzed for phenol concentration using UV spectrophotometer. The ranges of these variables are compiled and given in (Table.1).

Characterization of adsorbent material

The morphology of natural laterite as well as modified laterite powders were imaged using scanning electron microscopy (SEM). This analysis indicated interesting and important morphological features of laterite powder particles before and after

Nomenclature

A_T	Temkin constant	[L/g]
b_T	Temkin constant	[-]
C_e	Equilibrium concentration of adsorbate solution	[mg/L]
C_i	Initial concentration of adsorbate solution	[mg/L]
C_t	Concentration of adsorbate solution at a time t	[mg/L]
K_1	Pseudo-first order kinetic model	$[min^{-1}]$
K_2	Pseudo-second order kinetic model	$[(mg/g)^{-1}min^{-1}]$
K_F	Freundlich constant	[-]
K_L	Langmuir constant	[-]
n	Freundlich constant	[-]
b	Constant	[-]
q_e	Amount of adsorbate per unit mass of adsorbent at time t	[mg/g]
q_m	Langmuir constant	[-]
q_t	Amount of adsorbate per unit mass of adsorbent at time t	[mg/g]
q_s	Theoretical isotherm saturation capacity	[mg/g]
T	Temperature	[K]

acid-treatment. A low-resolution SEM image of the natural laterite powder is presented in (Fig. 1A). It can be seen that the natural powder particle surface constitutes a disintegrated network of little number of separated, cylindrical shape isolated pores (having circular cross-section) with an average size of 120 μM. Further, the high-resolution image (cf. Fig. 1B) clearly showed that the isolated pore structure (spotted with an open circle) was free of cracks, indicating the raw powder particles have a smoother surface. EDX spectrum (cf. Fig. 1C) of this high-resolution region (spotted with an open circle) displayed the elemental peaks of iron [Fe], aluminium [Al], as well as silicon [Si]owing to the coexistence of hematite, goethite, alumina, and quartz phases in laterite powder particles. Based on these microstructure evidences, the morphology of natural laterite powder particles can be best described as a collection of almost similar size isolated pores, unevenly distributed in the form of a disintegrated pore network inside the raw laterite particle surface. The morphological features of acid-treated laterite powder particles are presented in (Fig. 2). The low-resolution SEM image (cf. Fig. 2A) of modified laterite particle surface showed almost an integrated pore network of interconnecting cylindrical shape pores (having circular or elliptical cross-section) with a wider range of sizes between 10 and 100 μM. Further, the high-resolution image (cf. Fig. 2B) clearly displayed the appearance of cracks across the pore structure (spotted with an open square), indicating that the treated powder particles have a rugged surface. The assemblage of hematite, goethite, alumina, and quartz phases in modified laterite powder particles can be confirmed from the EDX analysis (of the high resolution region spotted with an open square, cf. Fig. 2C). Also, it has been observed that there is a considerable reduction in peak intensity for silicon [Si] in the EDX spectrum (cf. Fig. 2C) of modified laterite as compared to that of natural laterite (cf. Fig. 1C). Such a reduced peak intensity of silicon [Si] is due to the dissolution of a part of siliceous phases in hydrochloric acid (HCl) during the acid leaching (or treatment) of raw laterite powder. Based on these microstructure attributes, the morphology of modified laterite powder particles can be best demonstrated in such a way as a collection of wider sized interconnected pores, hierarchically distributed in the form of an integrated pore network inside the modified

laterite particle surface. The formation of such integrated continuous pore network on remarkable improvement in pore volume, surface area, as well as surface charge characteristics of modified laterite

powder particles can be strongly evidenced from the structural analysis data (cf. Table 2 and Fig. 3A & B). It can be noted as the high degree of hierarchically ordered pore structure promotes fast mass transfer kinetics, thereby enhancing the adsorption capacity significantly for modified laterite than that of natural laterite. In view of these key morphological attributes, the current work selects modified laterite powder as an adsorbent material to perform the adsorption process in a very effective manner. Preliminary studies also revealed that adsorption by natural laterite was insignificant whereas modified laterite exhibited significant levels of adsorption of phenol.

Table 1 — Parameters used in the study

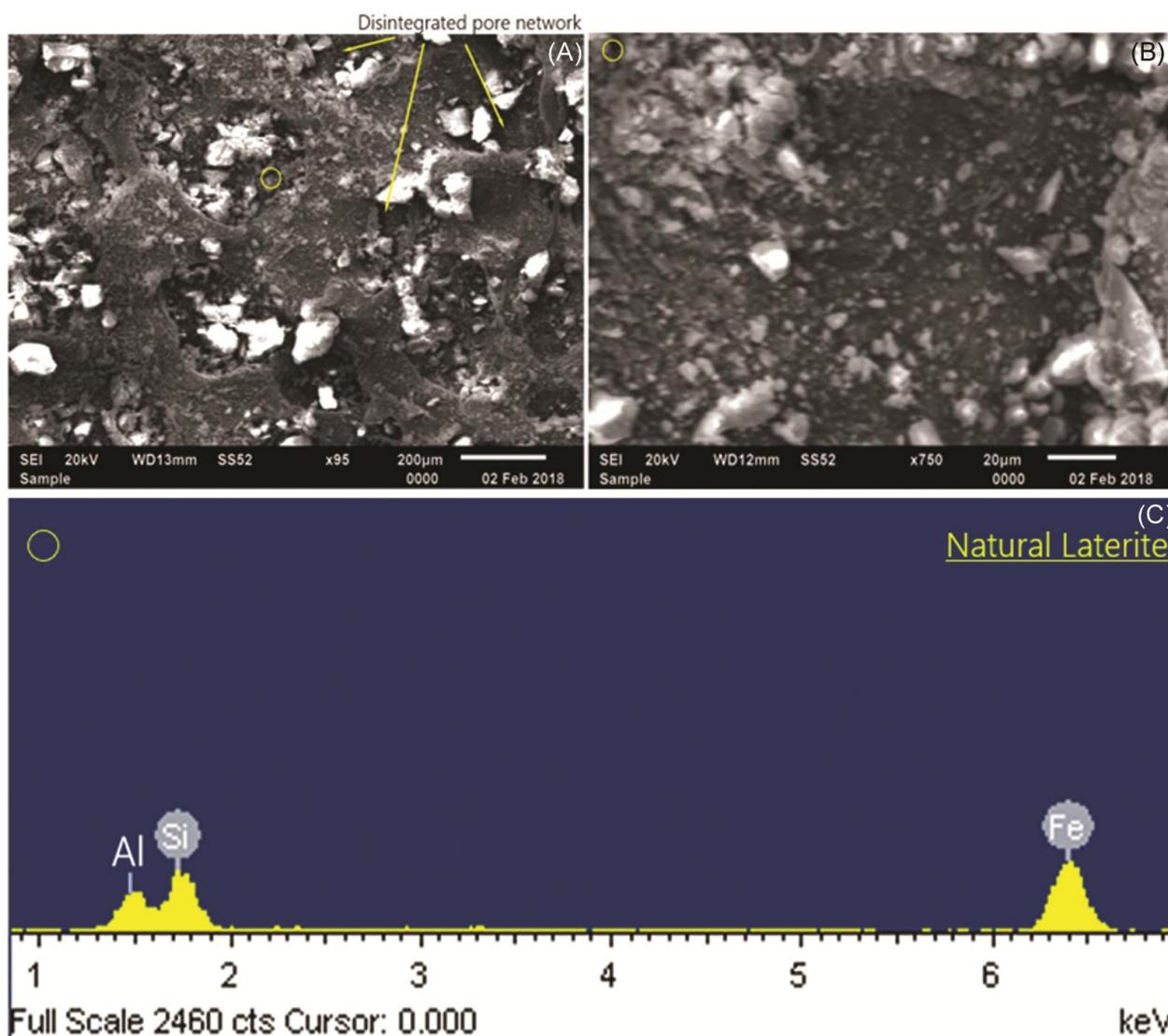| Sl. No.	Parameter	Range
1	Contact time (min)	0.0 – 60.0
2	pH	2.0 – 9.0
3	Initial concentration (mg/L)	2.0 – 300.0
4	Adsorbent dosage (g/L)	2.0 – 20.0

Fig. 1 — SEM morphology of the natural laterite powder: (A) low-resolution image shows a disintegrated pore network containing separate, isolated pores; (B) high-resolution image displays crack free regions across the pore structure, indicating that surface of the natural laterite powder particles is smooth; and (C) EDX analysis confirming the coexistence of hematite, goethite, alumina, as well as quartz phases in natural laterite
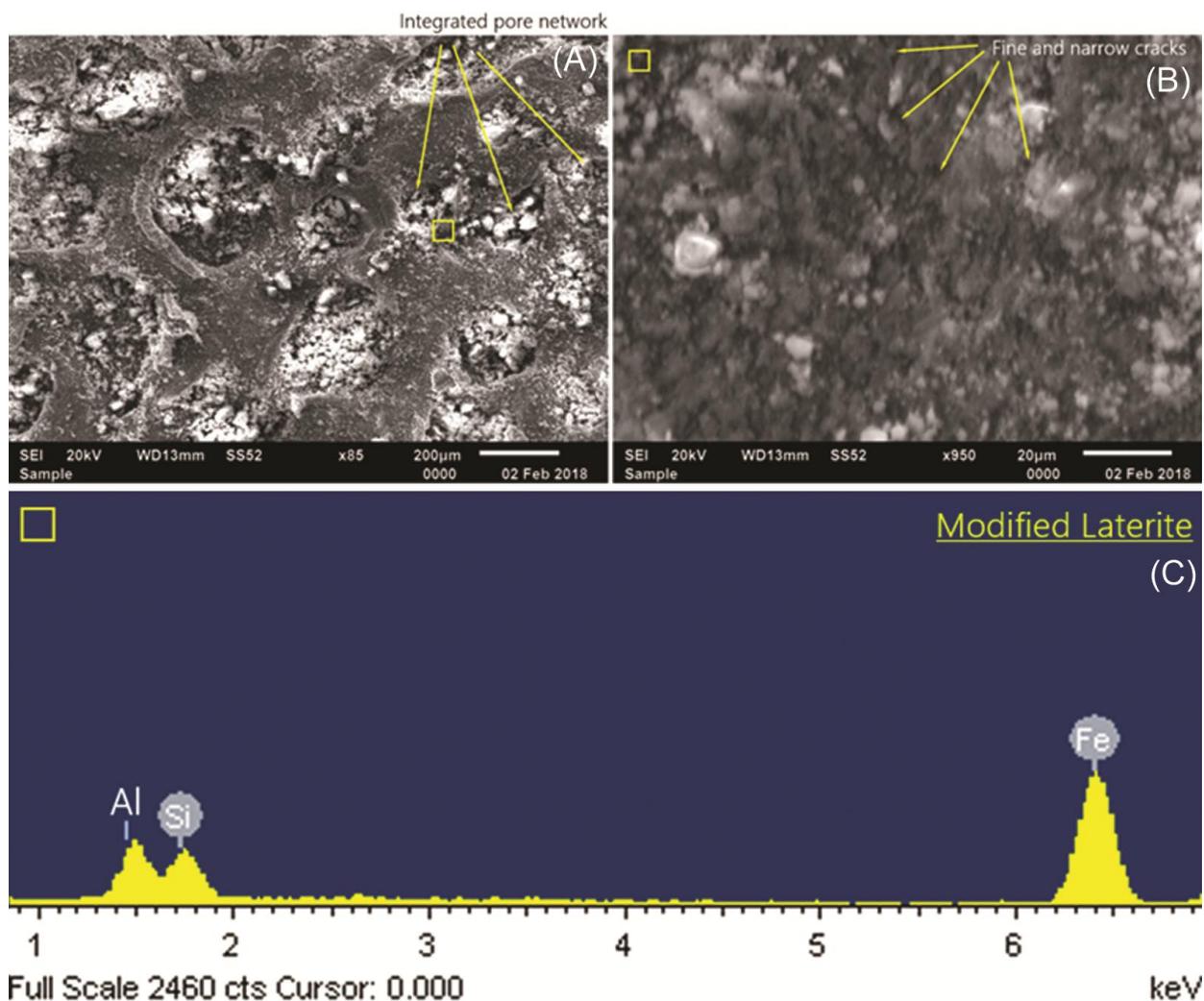
Fig. 2 — SEM morphology of the modified laterite powder: (A) low-resolution image shows an integrated pore network containing interconnecting pores; (B) high-resolution image displays cracked regions (with fine and narrow cracks) across the pore structure, indicating that surface of modified laterite powder particles is rough. The phase assemblage of hematite, goethite, as well as quartz in modified laterite can be confirmed from the EDX analysis. It can be noted that the reduction in intensity of elemental silicon [Si] peak is due to dissolution of a part of siliceous phases in hydrochloric acid (HCl) during the acid treatment of natural laterite powder

Results and Discussion

Absorption intake is calculated by using (Eq. 1).

$$\% \ of \ adsorption = \frac{C_i - C_t}{C_i} \times 100 \qquad \ldots (1)$$

Effect of Contact time

For the completion of the process within a short time, the effectiveness and efficiency of adsorption process is extremely important for industrial applications. The effect of contact time on adsorption of phenol was shown in (Fig. 4A). From the graph it was observed that the concentration of phenol unadsorbed in the solution gradually decreased and attained equilibrium after 120 min. After this period the removal of phenol *vs* time curves are smooth and continue leading to saturation. The concentration of phenol adsorbed at initial period was high due to the increase of number of vacant sites on the laterite available at the initial stage.

Effect of pH

The pH value of the solution plays an important role in the adsorption process and particularly on the adsorption capacity. The effect of pH on phenol adsorption was shown in (Fig. 4B) in which pH was varied from 2.0 to 10.0. From the graph it was observed that the optimum pH was around 3.0 at which

Table 2 — Physical properties of natural laterite and modified laterite including BET study

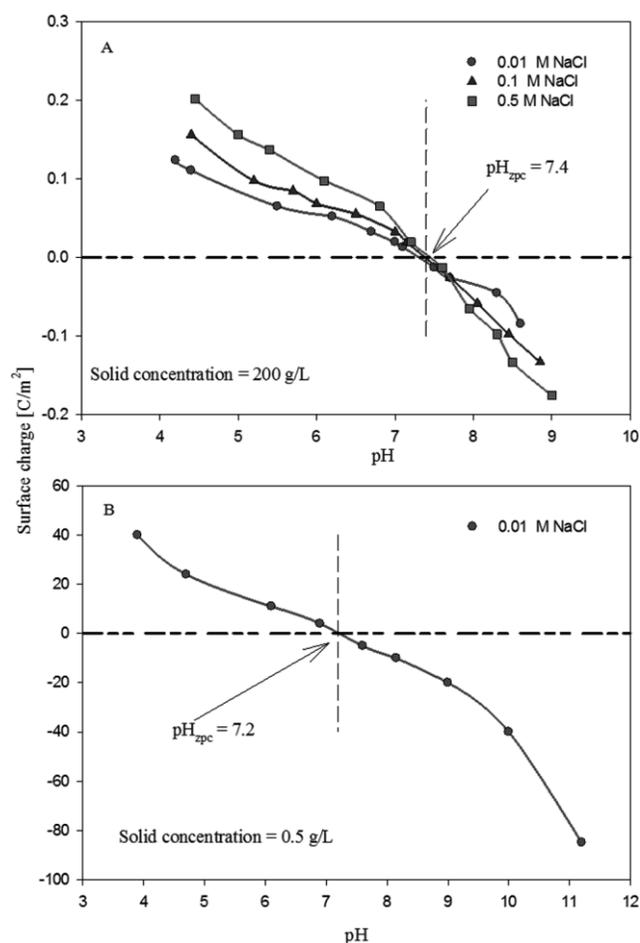| Property	Natural laterite	Modified laterite
Particle size, mM	0.25 – 0.5	0.25 – 0.5
Surface area, m^2/g	17.5	181.5
Total pore volume (BJH method), mL/g	0.020	0.35
Mesopore volume, mL/g	0.01	0.21
Micropore volume (HK method), mL/g	0.009	0.14
Bulk density, g/mL	1.36±0.05	1.08±0.03
True density, g/mL	2.46±0.01	1.90±0.02
Conductivity (1:5 laterite:water mixture), µS/cm	15.0±2.2	34.3±1.2
pH (1:5 laterite:water mixture)	6.65±0.02	7.2±0.2
pH_{zpc}	7.4±0.2	7.2±0.1
surface charge (at pH=7.0 and 0.01M Nacl), C/g	0.45±0.02	3.1±0.1
Inorganic composition as metal wt%		
Fe	49±2.5	51±2.6
Si	32.4±2.4	30.7±2.9
Al	14.4±1.2	12.5±1.1
Mn	1.9±0.4	1.6±0.5
Ti	~1.0	~1.0
K, Na, Ca	~1.0	~1.0

Fig. 3 — (A) Variation of the surface charge of natural laterite sample with pH for three different strengths of solution; and (B) Variation of the surface charge of modified laterite sample with pH

the maximum adsorption of phenol on laterite was found. From Figure 3B, it can be noticed that the surface charge is positive upto a pH value of 7.2 and negative beyond this value. At pH units beyond 10.0, phenol dissociates into negatively charged phenolate ions. Hence no adsorption exists for pH higher than 10.0. For pH range of 0 to 10, phenol appears in the neutral form. Being polar in nature, phenol appears as hydronium ion and deprotinated phenol molecules in the acidic range of pH upto 5. Beyond 5 and upto 10 units of pH, phenol appears predominantly in neutral form.

Effect of initial concentration

The effect of initial concentration on the amount of phenol adsorption was shown in (Fig. 4C). From the graph it was observed that the extent of phenol adsorption increases with increase in concentration of phenol and reached maximum at 200 mg/L. This is because at low concentration of phenol, most of the active sites are unoccupied at any given time. With increase in the concentration of phenol, the number of active sites occupied also increased. This was due to the fact that, the higher the initial phenol concentration, the greater the driving force of the concentration gradient at solid-liquid interface which cause an increase in the amount of phenol adsorbed on the laterite.

Effect of adsorbent dosage

The results of the present investigation carried out to explain the effect of adsorbent dosage were plotted against percentage of adsorption and shown in (Fig. 4D). An examination of the plot revealed that the adsorption was maximum at a dosage of 0.6 g. The results interpret that after the maximum dosage, it attains equilibrium due to which the active sites were not present and hence lower percentage of removal takes place at low dosage values.

Kinetic models

Both pseudo first order (Eq. 2) and pseudo second order (Eq. 3) kinetic models have been applied to
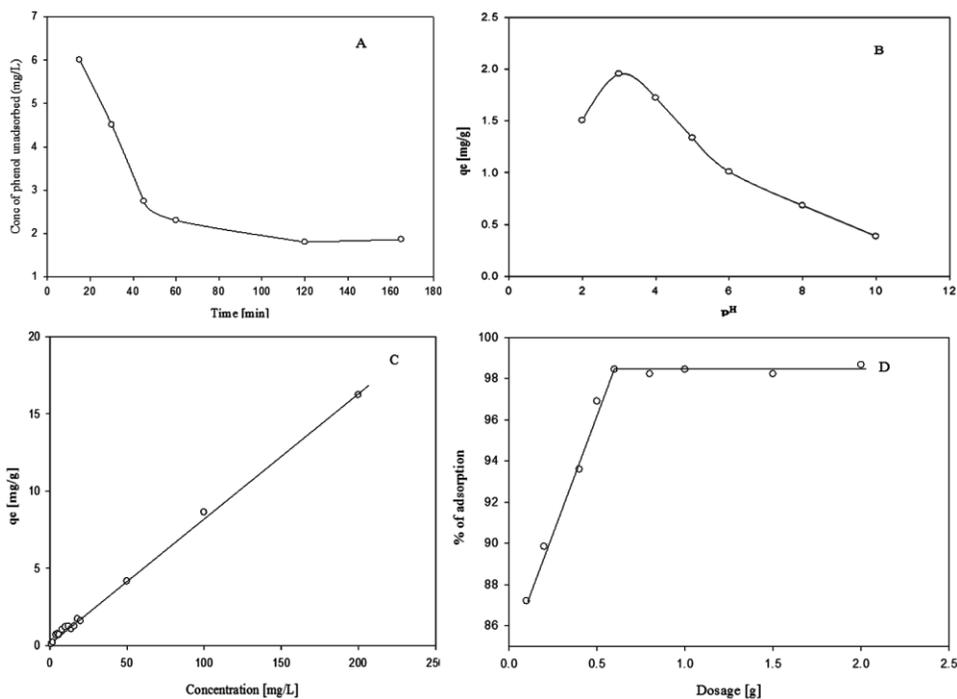
Fig. 4 — (A) Effect of contact time; (B) Effect of pH; (C) Effect of initial concentration; and (D) Effect of adsorbent dosage
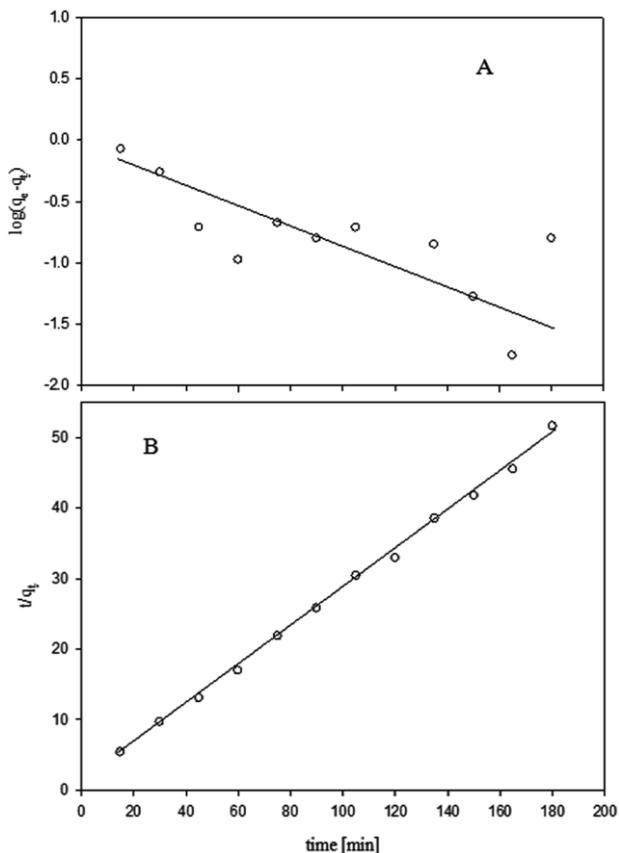

Fig. 5 — (A) Pseudo first order model; and (B) Pseudo second order model

the present data and the resulting graphs were shown in (Fig. 5A & B) respectively. Perusal of the plots of these figures reveals that pseudo second order model was in good agreement with the present data.

Pseudo 1st order model $\ln(q_e - q_t) = \ln(q_e) - K_1$ … (2)

Pseudo 2nd order model $\dfrac{t}{q_t} = \dfrac{1}{K_2 q_e^2} + \dfrac{1}{q_e} t$ … (3)

Adsorption isotherms

An adsorption isotherm represents a relationship between the amount of adsorbate that has been adsorbed at a constant temperature and its concentration in the equilibrium solution. It provides physiochemical data for assessing the applicability of the adsorption process as a complete unit operation. In our study, we assumed monolayer adsorption of phenol and applied the Freundlich (Eq. 4), Langmuir (Eq. 5) and Temkin (Eq. 6) isotherms to fit the equilibrium data of adsorption of phenol on laterite. The resulting graphs were shown in (Fig. 6A-C), respectively. Examination of the plots of these figures reveals that Freundlich isotherm model was in good agreement with the present data.

Freundlich isotherm $q_e = K_f C_e^{1/n}$ … (4)

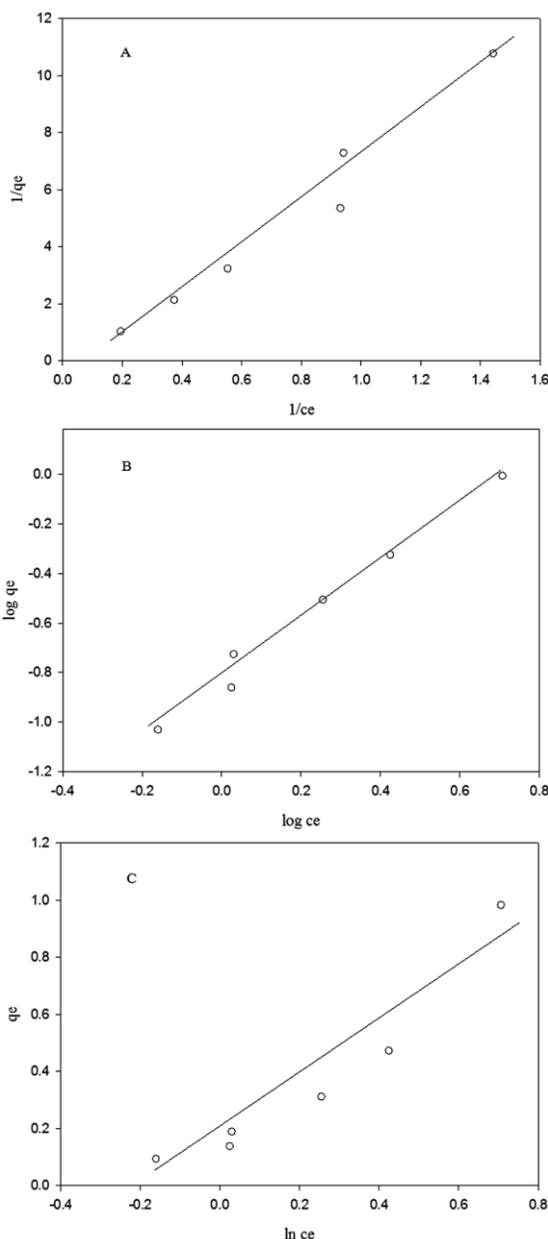Langmuir isotherm $q_e = \dfrac{q_m K_L C_e}{1 + K_L C_e}$ … (5)

Fig. 6 — Adsorption isotherms: (A) Freundlich; (B) Langmuir; and (C) Temkin

Temkin isotherm $\quad q_e = \dfrac{RT}{b_T} \ln(A_T C_e)$ $\qquad$ … (6)

Conclusion

The following conclusions were made from the experimental results and discussion of previous sections. Most favourable contact time is established as 120 min. Ideal pH value is 3.0 and best initial solution concentration is 200 mg/L for cadmium. Optimum adsorbent dosage value is found to be 6 g/L.

Pseudo 2nd order kinetic model was agreed well by the present data. Three isotherms *viz*., Langmuir, Freundlich and Temkin were examined and found that Freundlich was obeyed by the present data.

Conflicts of interest

All authors declare no conflict of interest.

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