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Adsorptive removal of phenol from coke-oven wastewater using Gondwana shale, India: experiment, modeling and optimization

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ABSTRACT

The aim of this study is to explore the effectiveness of Gondwana shale for the removal of phenol from coke-oven wastewater. The phenol concentration in coke-oven plant effluent varies from 2 mg/L to 10 mg/L depending on the extent of final treatment in the effluent treatment plant. Kinetics of the removal of phenol from industrial effluent having different initial phenol concentration using Gondwana shale has been studied in a batch contactor by varying different parameters. Morris Webber model has been found to fit the kinetic data. Langmuir isotherm model has been found to fit the equilibrium data with R^2 value of 0.986 and adsorption capacity q^0 of $0.0334\,\mathrm{mg\,g^{-1}}$. Response surface methodology has been employed to optimize the removal condition of phenol using shale. The spent shale obtained by removing phenol at optimum condition is used for recovery study. Finally, to see whether the shale is efficient with much higher concentration of phenol, it is contacted with untreated industrial wastewater coming directly from coke-oven battery in a batch contactor. 74.11% removal has been obtained after 24 h when 100 ml of industrial wastewater having phenol concentration of 476.24 mg/L was contacted with 50 g shale at pH 9.3.

Keywords: Adsorption; Response surface methodology; Coke-oven wastewater; Phenol; Gondwana shale

1. Introduction

Phenols are common contaminants found in effluents released from different industries such as petroleum refineries, coke-oven plants, paper, textile, pharmaceuticals, paint, ply wood, olive mill etc. [1–7]. Since phenol and its compounds are harmful to micro-organisms even at low concentrations and have several adverse effects on human health, they are considered as priority pollutants [8]. Human body parts quickly adsorb phenol through oral, inhalation and dermal route [9]. It is irritating to the eyes and skin upon direct contact. One of the major hazards of phenol is its ability to penetrate the skin rapidly [9]. Thus, it is necessary to eliminate phenols from industrial wastewater before it is discharged to environment. According to the US environmental protection agency regulation, the phenol concentration in wastewater should be less than 1 mg/L [2]. Several methods such as microbial degradation, chemical oxidation,

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chemisorptive removal, ion exchange, photochemical conversion, catalytic oxidation etc. have been proposed for the removal of phenols from its aqueous solution of which adsorption, being technologically simple, cost effective and environmental friendly, can be considered as better alternative for the treatment of phenol laden wastewater to meet the environmental regulations [1–7,10–12]. Though activated carbon is the most widely used adsorbent because of its high adsorption capacity for organic compounds, its use is usually limited due to its high initial and regeneration cost [7]. Thus, researches are now tending toward the searching of low cost or natural adsorbents. Some of the worth-mentioning studies in the field of adsorption use different cheap adsorbents like hen feathers, coconut husk, bottom ash, de-oiled soya, egg shell waste [13–23]. In this study, the adsorption capacity of Gondwana shale in removing phenol from industrial wastewater has been examined.

Shale is a sedimentary rock composed of clay (<1/256 mm or <2 μm) size particles of different minerals. Shale is a generic term representing a particular sedimentary rock formed under specific range of palaeoenvironmental setting in geologic past. The adsorptive and/or absorptive properties of shale are the manifestation of combined physicochemical effect of various clays present in the rock. Though few works have been done to remove several pollutants using clay materials [24–26], as far the knowledge of present research group concerned, no study has been made in removing organic pollutants using Gondwana shale till date.

Gondwana shale, used in this study, itself is a mine waste generated as removed overburden in coal mines. The abundance of shale in earth's crust and its low cost make it a strong contender as an adsorbent for the removal of pollutants from wastewater. Gondwana coal is rich in West Bengal, a province in India. In this work, industrial effluents were collected from coke-oven plants situated at the industrial city Durgapur, which is the hub of plethora of industries like integrated steel plants, power plants, chemical industries, cement industries, etc. The treated or untreated effluents of most of the industries are released through unlined drains to a storm water stream, Tamla Nalla, which ultimately finds its way to Damodar river flowing toward east along the southern margin of the city. Thus, if these effluents are not treated properly before being discharged to storm water streams, there is enough possibility of severe pollution of surface water and ground water. To assess this, the effluent from nearby coke-oven plant was collected and analyzed. The results show that the concentration of phenol lies in the range of 2–10 mg/L, which is far beyond the statutory limit as prescribed by several agencies. It can be said, therefore, that the technologies which are presently being used by the industries are not sufficient to reduce the pollutant level below standard limit and a polishing step is mandatory. In the present investigation, an attempt has been made to explore the potential of Gondwana shale, obtained from Raniganj coal fields (West Bengal), in removing phenol from this effluent which serves the dual purpose of the utilization of mine waste and minimization of phenol from wastewater. Here lies the novelty and significance of the present work.

To ascertain the adsorption mechanism of phenol from effluents of coke-oven plant by Gondwana shale and to establish the kinetics of phenol removal, a thorough kinetic study is carried out by changing different process variables. Equilibrium study is performed to evaluate the extent of phenol adsorption by Gondwana shale. As far as known, no work has been made so far to optimize the process condition for the adsorptive removal of phenol by response surface methodology (RSM). Thus, in the present investigation, RSM is used to model and optimize the adsorptive removal of phenol from coke-oven wastewater. Recovery study of phenol has been performed with the spent shale obtained by removing phenol at optimum condition which gave an insight on the reusability of spent adsorbent. RSM is employed here to optimize the recovery of phenol. Finally, to establish the effectiveness of the shale in treating wastewater containing much higher concentration of phenol, shale has been contacted with untreated raw effluents coming out from coke-oven battery of the same coke-oven plant. The result has been found satisfactory.

2. Materials and methods

2.1. Collection of Gondwana shale and its preparation

Gondwana shale blocks were obtained in the form of solid rocks from the open cast mines of Mahabir colliery, Raniganj (West Bengal) (23˚36´58´´ N and 87˚06´ 19´´ E), India. All the shale blocks were first crushed using a jaw crusher and then finally ground in a ball mill. The ground materials were subjected to grain size analysis through sieving. The size of the grains range from 90 μ (−150 BSS + 200 BSS) to 168.5 μ (−72 BSS + 120 BSS) and were used as the adsorbent of phenol.

2.2. Characterization of Gondwana shale

The characterization of Gondwana shale, obtained from Mahabir Colliery, Raniganj (West Bengal), India, was done following standard protocol [10]. The physicochemical properties determined include solid density, bulk density, Kjeldahl nitrogen, total organic carbon (TOC), etc. Surface area of Gondwana shale was estimated by BET method. M/s Quantachrome make NOVA 4000e (USA) was used for such purpose. For the determination of pore volume, mercury intrusion method was applied. M/s Quantachrome make Poremaster 60 (USA) was employed for the measurement of pore volume. For the evaluation of all these properties, the particles with 90 μ size were used. Scanning electron microscope (SEM) studies of Gondwana shale before and after adsorption of phenol were carried out to acquire their morphological/topographical characteristics. The samples were placed on brass stubs using adhesive tape. SEM (M/s HITACHI—S −3000 N, Japan) was used to take SEM photographs at the specified magnification. 25 mm was kept as working distance and 15 kV acceleration voltages were used. Secondary electron image was used as a detector. X-ray diffraction of Gondwana shale was carried out to obtain its crystal structure with the M/s Philips PANalytical X-Pert Diffractometer, Cu Kα radiation ($\lambda = 0.154056$ nm).

FTIR study of shale was conducted with the help of Fourier Transform Infra Red machine (M/s Nicolet iS10, Thermo Fischer Scientific, USA). For the FTIR study, 2 mg of finely ground adsorbent was mixed well with approximately 40 mg of KBr for the preparation of transparent pellets, from which functional group was determined.

2.3. Characterization of coke-oven wastewater

Samples of treated wastewater were collected from outfall of nearby coke-oven plant at Durgapur and samples of untreated raw wastewater water were collected directly from coke-oven battery of the same coke-oven plant throughout the year. The parameters like pH, color, odor, COD, ammoniacal nitrogen, and phenol were analyzed. The concentration of phenol in treated wastewater and raw wastewater was found to be in the range of 2–10 mg/L and 400–476.24 mg/L, respectively.

2.4. Removal of phenol using Gondwana shale

2.4.1. Kinetic study for the removal of phenol from treated wastewater

The treated wastewater collected from the outfall was found to contain phenol in the range of 2–10 mg/L and has been used as such owing to its clear nature. However, for the variation of initial concentration of phenol, dilution with distilled water was done wherever required. To establish the kinetics of phenol removal from treated wastewater by Gondwana shale, a comprehensive kinetic study was performed by changing three input parameters viz., pH (7–9), weight of shale (1–3 g) and the size of the shale (90–168.5 μ) in a prescribed manner. Wastewater containing different concentration of phenol was stirred with a definite weight of shale sample obtained from Mahabir colliery having specific particle size in a batch contactor placed in a BOD incubator with shaker (Digitech Systems, India) at 30˚C. The samples were taken out of the shaker after particular time intervals and were filtered by vacuum filter using membrane filter paper of pore size 0.45 μ and the residual phenol concentrations were determined by the 4-aminoantipyrine method by means of UV-Visible Spectrophotometer (M/s UV 2,300, TECHCOM) at 500 nm [27].

2.4.2. Equilibrium study for the removal of phenol

For equilibrium study, 100 ml of wastewater having the concentration of phenol in the range of 0.5 to 10.0 mg/L, prepared by the dilution of treated industrial wastewater with definite amount of distilled water (if required), was used. These were contacted with 3.5 g of shale taken in the flasks. The flasks were closed and placed for 24 h in a BOD incubator with shaker maintained at 30˚C. Finally, the mixtures were taken out of the shaker after particular time intervals and were filtered by vacuum filter using membrane filter paper of pore size 0.45 μ, and the filtrate was analyzed spectrophotometrically at 500 nm.

2.4.3. Optimization of phenol removal using Gondwana shale by RSM

Experimental. From kinetic study of phenol removal using Gondwana shale in a contactor, it is found that the smallest size of shale has the highest removal efficacy. Therefore, during optimization through response surface methodology (RSM), all the experiments were performed using 90-μ-sized particles. Four input parameters, such as initial concentration of phenol, amount of shale, pH and temperature, were taken as numeric input factors and percentage removal of phenol as response. Design Expert Software 8.0.1 was used to design the experiments. The initial concentrations of solution, amount of shale, pH and temperature were varied according to the experimental design as shown in Table 1. The concentration and pH of wastewater were adjusted to meet the requirement of the design as provided by the software. Kinetic study shows that percentage removal of phenol reaches to its equilibrium at about 22 h. Therefore, for the

Table 1
Experimental design for removal of phenol

Sl. no.	Initial concentration of phenol (A_1, mg/L)	Weight of shale (B_1, g)	pH (C_1)	Temperature (D_1, °C)	Removal of phenol, (R_1, %)
1	0.5	3.5	7	30	41.0
2	3	2	5	35	58.3
3	3	2	9	25	53.9
4	3	2	5	25	54.2
5	3	2	9	35	57.8
6	3	5	5	35	78.3
7	3	5	9	25	63.5
8	3	5	9	35	64.7
9	3	5	5	25	70.4
10	5.5	3.5	7	30	80.2
11	5.5	3.5	7	30	80.2
12	5.5	0.5	7	30	57.3
13	5.5	3.5	7	30	80.2
14	5.5	3.5	7	30	80.2
15	5.5	3.5	7	40	82.7
16	5.5	3.5	3	30	78.5
17	5.5	3.5	7	30	80.2
18	5.5	6.5	7	30	92.8
19	5.5	3.5	7	30	80.2
20	5.5	3.5	7	20	76.1
21	5.5	3.5	11	30	67.5
22	8	2	9	35	81.3
23	8	2	5	25	78.8
24	8	5	5	25	91.3
25	8	2	5	35	84.2
26	8	5	5	35	94.3
27	8	5	9	25	91.0
28	8	5	9	35	92.2
29	8	2	9	25	79.3
30	10.5	3.5	7	30	91.6

optimization of process parameters of phenol removal, run time was fixed at 24 h. Two hundred millilitres of phenol solution having definite concentration was contacted with definite amount of Gondwana shale in a batch adsorber for 24 h. The residual phenol concentration in solution was measured.

Design of experiments. RSM is based on the three steps viz., (1) performing the experiments which have been designed statistically; (2) prediction of the model equation and estimation of its coefficients for determination of response, and (3) verification of the precision of the model [28]. RSM assists to enumerate the relationships between theoretically predicted responses and the fundamental input parameters [28,29].

$$y = f(x_1, x_2, \cdots, x_n) \tag{1}$$

where

y = the response, $x_1, x_2, \cdots, x_n$ = input parameters.

Hameed et al. and Sahu et al. [28,30] showed that number of experiments to be performed depends on the number of input parameters. A general expression of the following form as used by them is

$$N = 2^n + 2n + n_c \tag{2}$$

where

n = number of factors, n_c = center point, N = the total number of experiments required.

If $n = 3$, the total number of experiments to be performed is 20, whereas if $n = 4$, total number of experiment becomes 30.

The experimental order was randomized to reduce the effect of the uncontrolled factors [31]. The results of all runs were examined, and an empirical second-degree polynomial equation, represented by Eq. (3), has been proposed to correlate the responses with four independent parameters for the removal of phenol by Gondwana shale [28–29,31–33].

$$y = a_0 + \sum_{i=1}^{n} a_i x_i + \sum_{i=1}^{n} a_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} a_{ij} x_i x_j \tag{3}$$

where

x_i = fundamental input parameters called factors, a_0 = constant coefficient, a_i = linear coefficient, a_{ii} = quadratic coefficients, a_{ij} = interaction coefficients.

ANOVA was used to optimize the parameters. The minimum (−1) and maximum (+1) level of four numeric factors viz., initial concentration of phenol, weight of shale, pH, and temperature of solution were 3 and 8 mg/L, 2 and 5 g, 5 and 9 and 25 and 35°C, respectively. Experimental design with the values of responses is presented in Table 1. The removal of phenol with initial concentration 8 mg/L, weight of shale 2 g, at pH 9 and 30°C temperature has been found to be optimum. The spent shale obtained by removing phenol at this optimum condition is used for recovery study.

2.4.4. Recovery of phenol from spent shale

Recovery of phenol was carried out by contacting spent shale with distilled water at various pH conditions. The volume of solution was maintained 350 ml in each case. *RSM* was employed to model statistically, optimize, and examine the conjugate effect of process variables for the recovery of phenol. Weight of spent shale, pH of solution, and time were considered as input factors, whereas percentage recovery as response. pH of solution was maintained using 0.1 (N) NaOH and 0.1 (N) HCl solutions. NaOH and HCl were procured from M/s. Merck, India. The maximum (+1) and minimum (−1) levels of weight of spent shale, pH, and contact time were 2 and 4 g, 5 and 9 and 24 and 36 h, respectively.

2.4.5. *Removal of phenol from untreated industrial wastewater using Gondwana shale*

Again to ascertain the effectiveness of Gondwana shale in the removal of phenol at higher concentration, untreated wastewater, collected directly from coke-oven battery of the same coke-oven plant, was used. The untreated water was turbid, so all the analyses were carried out after leaving wastewater for 24 h to settle down all the dust particles. One hundred millilitres of this raw wastewater was contacted with 50 g of Gondwana shale having size 90 µ in a batch contactor placed in a BOD incubator with shaker (M/s. Digitech Systems, India) at 30˚C. To assess effect of pH on the removal efficacy of shale at higher concentration of phenol, kinetic studies were carried out at two different pH conditions such as untreated wastewater at its own pH and at pH 7. Samples were collected at definite time intervals and analyzed for residual phenol concentration.

3. Results and discussions

3.1. *Characterization of Gondwana shale*

Gondwana shale obtained from Mahabir Colliery, Raniganj (West Bengal) (23˚36′58′′ N and 87˚06′19′′ E), India, is characterized in terms of bulk density, solid density, Kjeldahl nitrogen, TOC, BET surface area and pore volume etc., as shown in Table 2. Higher value of solid density refers to the presence of more mass vis-à-vis more amount of clay minerals per unit volume which favors the adsorption process. In the present study, solid density (2054 kg m^{-3}) has been found to be more than bulk density (2000 kg m^{-3}).

SEM images of Gondwana shale before and after the adsorption of phenol have been shown in Fig. 1(a) and (b), respectively. It is evident from these figures that the surface of Gondwana shale in its native form is very much uneven with microporous structure, whereas after the adsorption of phenol, the surface becomes very smooth. On contacting phenol solution with shale, adsorbate (phenol) molecules are bound to the pores of the adsorbent (shale) and thereby making its surface smoother indicating adsorption of phenol on it. Thus, the adsorptive ability of Gondwana shale has been primarily established.

Average interplanar distance and the average composition of the mineral phases can be derived from XRD. The spectrum obtained from XRD study (Fig. 2(a)) of the shale sample shows the minerals like chlorite ($HMgO_3Si$, $AlFeO_3Si$), Siderite ($FeCO_3$; rhombohedral crystal system), Kaolinite ($Al_2Si_2O_5(OH)_4$; anorthic crystal system), Montmorillonite ($NaMgAlSiO_2(OH)H_2O$; and $Si_{3.74}Al_{2.03}Fe_{0.03}Mg_{0.02}O_{11}$), Quartz ($SiO_2$; Hexagonal), Sodium salicylate ($C_7H_5NaO_3$),

Table 2
Physicochemical characterization of shale and treated coke oven waste water

Characterization of shale		Characterization of treated coke oven waste water	
Parameters	Values	Parameters	Values
Solid density (kg/m^3)	2054	Colour	Straw
Bulk density (kg/m^3)	2000	Odour	Obnoxious
Kjeldahl nitrogen (mg L^{-1})	8.4	pH	9
Total organic carbon (%)	2.329	COD (mg/L)	226
BET surface area (m^2/g)	11.02	Ammoniacal nitrogen (mg/L)	437
Pore volume (cc/g)	0.4147	Phenol (mg/L)	2–10

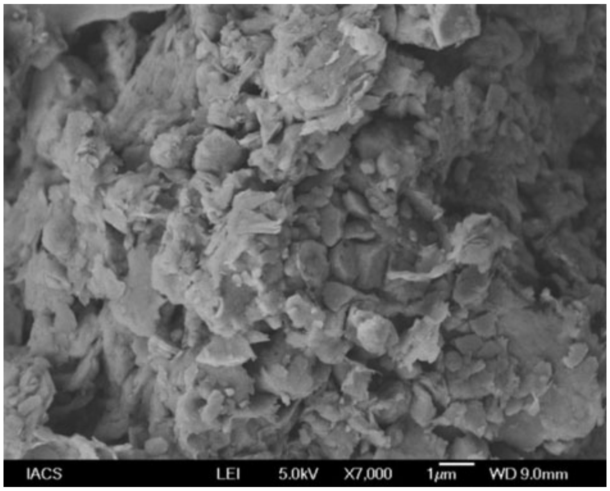

Fig. 1(a). Scanning electron micrograph of shale before adsorption of phenol.

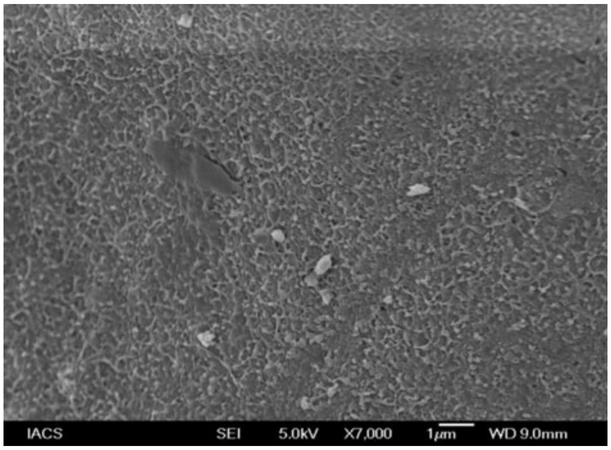

Fig. 1(b). Scanning electron micrograph of shale after adsorption of phenol.

Tridymite (SiO_2; orthorhombic crystal system), in the form of characteristic peaks. Montmorillonite found from XRD studies is an expandable clay and thus acts as a good adsorbent.

Fig. 2(b) represents the FTIR spectrum plots obtained from Gondwana shale before and after the adsorption of phenol. The results of FTIR are quite helpful in the identification of functional groups and stretching frequencies. The results of FTIR exhibit that the functional group found in the shale is hydroxyl and shale is pure in nature. The stretching frequencies (cm^{-1}) of the bonds were found as follows: 468.92 (Si–O–Fe), 537.24 (Si-O-Al), 694.92 (Si-O-Al), 797.57{(Al, Mg)–O-H}, 913.00 (Al–OH), 1,032 (Si-O-Si), 3447.79 (H-O-H), 3619.89 (Al–OH), 3691.40 (Al–OH). Peaks from 3,200–3,500 and 3,580–3,650 cm^{-1}usually detect the presence of phenolic compounds (or hydroxyl compounds). There has been shift in absorption peak from 3447.79 to 3447.88 cm^{-1} (H-O-H) and from 3650.41 to 3650.44 cm^{-1}(O-H) in shale and phenol adsorbed shale, respectively. So, the adsorption of phenol has again been proved.

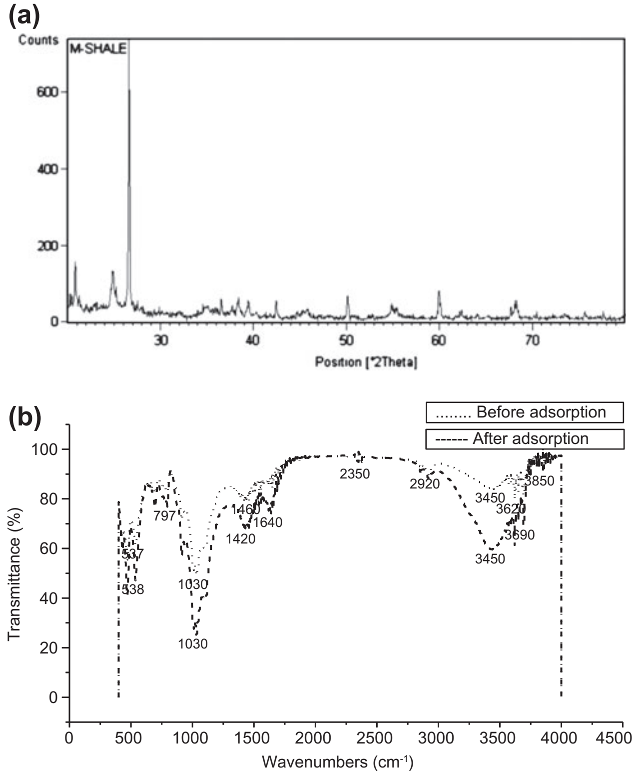

Fig. 2. (a) XRD patterns of shale and (b) FTIR results of shale and shale adsorbed with phenol.

3.2. The removal of phenol using Gondwana shale

3.2.1. Kinetic study for the removal of phenol from treated wastewater

The physicochemical properties of treated industrial waste-water collected from outfall of nearby coke-oven plant is given in Table 2. To ascertain the kinetics of phenol adsorption, a comprehensive kinetic study was carried out with treated wastewater having phenol concentration in the range of 2–10 mg/L. Other process parameters, such as pH (7–9), weight of shale (1–3 g) and the size of the shale (90–168.5 μ), have been varied in a judicial manner. Results show that the removal process took 22 h in every case to reach its saturation level. Maximum removal (99.9%) of phenol was obtained when wastewater containing 6 mg/L phenol was contacted with 2 g of shale with size 90 μ at 30°C at its own pH (pH 9).

Percentage removal-time histories of phenol has been plotted in Fig. 3(a) varying pH (7 and 9), keeping all other parameters like initial concentration, amount of shale, size of shale and temperature constant at 6 mg/L, 2 g, 90 μ and 30°C, respectively. The figure reveals that the percentage removal is same (99.9%) at both pH 7 and 9. As is evident from the Fig. 3(a), the percentage removal of phenol has been increasing with time at both the pH. There has been a consistent removal of phenol vis-à-vis mass transfer up to 8 h. The reason may be attributed to the high concentration of phenol at initial stage of removal. Sixty-two percent of phenol removal has been observed at about 8 h at both the pH. After 8 h, there has been a decrease in rate of removal of phenol which again increases after 15 h. The probable mechanism of adsorption of phenol on shale may be due to the formation of hydrogen bond between the hydroxyl group of phenol and the hydroxyl group of shale. This interaction is ionic in nature and depends mainly on pH of solution. There may be difference in interaction between the adsorbent and adsorbate molecules at various pH, and thus, resulting in irregularity of the removal of phenol which is trivial in nature. Since there is no significant change in percentage removal of phenol with change in pH, all the kinetic studies with wastewater have been performed at its own pH. This makes the process cost-effective.

Fig. 3(b) shows the kinetics of phenol removal from treated wastewater considering initial concentration of phenol as a varying parameter keeping all other parameters like amount of shale, size of shale and temperature constant at 2 g, 112.5 μ and 30˚C, respectively. As is evident from the figure, the removal at 2 and 10 mg/L are consistently increasing with time. Initially, the removal of phenol with 5 mg/L solution followed the same pattern as that of 10 mg/L. At the end of 8 h, 16.4% phenol removal has been achieved, and after about 15 h, it regains its original trend of increasing with time. For higher initial concentration of phenol at 10 mg/L, an appreciable amount 85.2% has been removed, whereas for the same operating condition only 55.5% removal is obtained when initial concentration is low as 2 mg/L. This may be due to the prevailing driving force for mass transfer, which is expressed as the difference between the bulk concentration of solute in the solution and that at the surface of the solid. The mass transfer driving force is greater with higher concentration of phenol than the lower one, when all other parameters are constant. This will be true only when the adsorption process is diffusion rate limited instead of reaction rate limited.

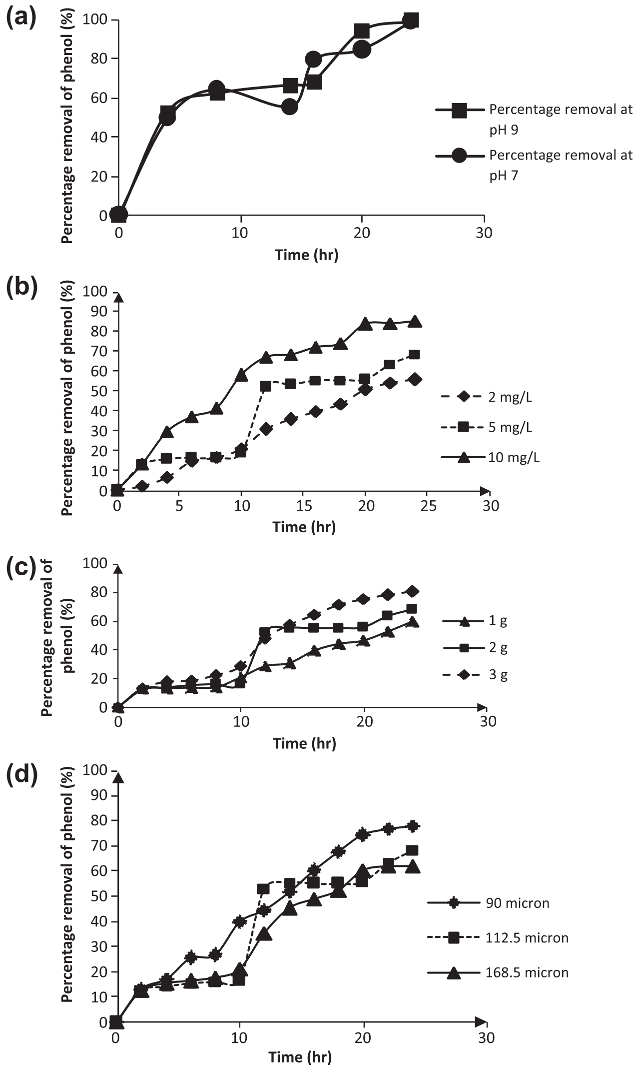

Fig. 3. Time series of percentage removal of phenol with (a) pH as parameter, (b) initial concentration of phenol as parameter, (c) weight of shale as parameter and (d) size of shale as parameter.

To ascertain the outcome of variation of weight of shale on extent of adsorption of phenol, the percentage removal has been plotted against time in Fig. 3(c) by changing the amount of shale from 1 to 3 g keeping other parameters constant such as initial concentration of phenol: 5 mg/L, size of adsorbent: 112.5 μ and temperature: 30˚C. Fig. 3(c) shows that the percentage removal of phenol increases with increase in adsorbent dosage. Higher removal (80.6%) is achieved with higher amount of shale (3 g). This may be because of the fact that more the amount of adsorbent, more is the availability of surface area for contact facilitating the adsorption process which is very much a surface phenomenon. The rate of removal of phenol with 2 g of shale decreases at about 10 h, and it increases again after 15 h.

Fig. 3(d) represents the percentage removal—time series of phenol when the size of Gondwana shale varies from 90 to 168.5 μ, respectively. The other parameters, such as initial concentration of phenol, amount of shale, and temperature, are kept constant at 5 mg/L, 2 g and 30˚C, respectively. Fig. 3(d) shows that increase in particle size results in decrease in the removal of phenol. Smaller size provides bigger surface area, means greater adsorption. Thus, removal of phenol increases with decrease in size of particles. The percentage removal of phenol with particle size 90 and 168.5 μ increases consistently throughout the experimental run. Till 10 h, the percentage removal of phenol with 112.5 μ has been comparable with that of 168.5 μ. At the end of 15 h, the percentage removal of phenol with 112.5 μ again starts to increase and remains as an intermediate between the smallest and biggest particle size. Higher removal of phenol (78.2%) is achieved with shale particles of smaller size (90 μ).

The effectiveness of Gondwana shale in removing phenol from wastewater may be attributed to its structure. The probable mechanism of the adsorption of phenol may be due to the formation of hydrogen bond between the hydroxyl group of phenol and the hydroxyl group projecting outward from the silica tetrahedral surface of clay minerals present in shale as suggested by Djebbar et al. (Fig. 4) [34].

Three kinetic models viz., pseudo second order model (PSOM), the Lagergren model, and Morris Weber model are employed for examining the kinetic data obtained experimentally in batch mode of operation.

Lagergren first-order kinetic model recommends a first-order kinetic rate based on surface reaction [35–36]. The following equation describes the model:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{4}$$

where

q_e = Solid-phase concentration of adsorbate at equilibrium, (mg/g), q_t = Solid-phase concentration at time t, (mg/g), k_1 = Rate constant of pseudo-first-order kinetics as used in Eq. (4), (hr^{-1}), t = Time, (h).

In PSOM, sorption process is considered as pseudo-second order in nature, and the rate-limiting step is of chemisorption in nature [29,35–36]. The mechanism may involve valence forces by sharing or through the exchange of electrons between sorbent and sorbate [36]. The following equation can be derived for this model:

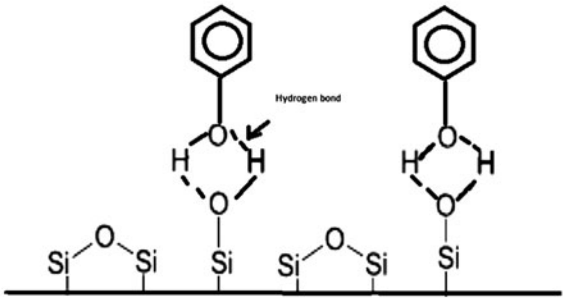

Fig. 4. Probable mechanism of adsorption of phenol on silica tetrahedral surface.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where

k_2 = Rate constant of pseudo-second order model used in Eq. (5), (g/mg h).

Morris Weber model assumes that if intraparticle diffusion is involved in the sorption process, then a plot of the square root of time vs. the uptake would result in a linear relationship [35,36]. If this line passes through the origin, then intraparticle diffusion would be the rate-controlling step of the sorption process [35,36]. The following is the equation for Morris Weber model:

$$q_t = k_3 t^{1/2} \tag{6}$$

where

k_3 = Intraparticle diffusion rate constant as used in Eq. (6), mg/(g hr$^{1/2}$).

Analysis of these three models reveal that Morris Weber model fits more accurately with the data obtained experimentally in the kinetic study by varying the initial concentration of phenol (2–10 mg/L), size of shale (90–168.5 μ) and amount of shale (1–3 g) as represented in Fig. 3(b)–(d) than the other two models. Results reveal that the nature of the adsorption process is of intraparticle diffusion limited which has already been diagnosed. The kinetic parameters are given in Table 3. Three different k_3 values are obtained when three input parameters viz., initial concentration,

Table 3
Values of kinetic parameters

Model equation	Parameters varied		
	Initial concentration of phenol (mg/L)	Weight of shale (g)	Size of shale (μ)
Lagergren equation	$k_1 = 0.161$	$k_1 = 0.171$	$k_1 = 0.122$
$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$	$R^2 = 0.88$	$R^2 = 0.831$	$R^2 = 0.907$
Pseudo-second-order model equation	$k_2 = 0.005$	$k_2 = 0.030$	$k_2 = 0.047$
$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$R^2 = 0.045$	$R^2 = 0.464$	$R^2 = 0.924$
Morris Weber equation	$k_3 = 0.038$	$k_3 = 0.052$	$k_3 = 0.015$
$q_t = K_3 t^{1/2}$	$R^2 = 0.924$	$R^2 = 0.964$	$R^2 = 0.979$

weight of adsorbent, and size of shale have been varied. To select the $k_{3,}$ suitable for practical application and examine the accuracy of results root mean square error (RMSE) has been used. RMSE is defined as RMSE $=\sqrt{\frac{\sum(q_{\exp}-q_{theo})^2}{N^1}}$, where $q_{\exp}$ = experimental solid phase concentration at different time intervals, q_{theo} = theoretical solid-phase concentration at different time intervals and N^1 = number of observations. RMSE has been found to be 0.0271, 0, and 4.00617×10^{-18}, respectively, when initial concentration of phenol, weight of shale, and particle size has been varied individually as a parameter. As the lowest value of RMSE is obtained with weight of shale, the corresponding k_3 value, that is, 0.052 mg/ (g h$^{1/2}$) has been chosen to be used in practical application**.**

3.2.2. *Equilibrium study for the removal of phenol from treated wastewater*

The data derived from equilibrium study are analyzed by fitting them in two adsorption isotherm models as Freundlich adsorption isotherm model $\left(q_e = K_F C_e^{\frac{1}{n'}}\right)$ and Langmuir adsorption isotherm model $\left(q_e = \frac{q^0 C_e K_L}{(1+K_L C_e)}\right)$.
where

q^0 = Solid-phase concentration of adsorbate for complete monolayer formation, (mg/g), C_e = Equilibrium concentration of phenol in solution after adsorption, (mg/L), K_L = Adsorption equilibrium constant used in Langmuir isotherm, (L/mg adsorbate), n' = Freundlich intensity parameter, K_F = Adsorption equilibrium constant used in Freundlich adsorption isotherm model, (mg adsorbate/g shale)/(mg adsorbate/L)$^{1/n'}$.

The equilibrium parameters of these two models are evaluated. For Langmuir isotherm model, the solid-phase concentration of adsorbate (phenol) q^0 = 0.0334 mg/g and the adsorption equilibrium constant K_L = 0.67569 (L/mg adsorbate) with R^2 = 0.986. For Freundlich isotherm model, the adsorption equilibrium constant K_F = 0.0118 (mg adsorbate/g shale)/(mg adsorbate/L)$^{1/n'}$ and Freundlich intensity parameter, n' = 2.439 with R^2 = 0.881. It is apparent from the values that equilibrium data for phenol adsorption fits more satisfactorily to Langmuir model than any other model. Fitting of data to Langmuir adsorption isotherm model reveals monolayer physical adsorption. It also entails no interaction between adsorbate molecules. All surface sites are equivalent, and the surface is uniform and the ability of a molecule to adsorb at the given site is independent of the neighboring sites.

3.2.3. *Optimization of phenol removal using Gondwana shale by RSM*

RSM is employed to determine the conjugate effect of various input parameters for the removal of phenol by Gondwana shale in addition to optimize the process condition. The input parameters, such as, initial concentration of phenol, weight of shale, pH, and temperature of the solution, are taken into consideration as numeric factors. The percentage removal of phenol is taken as response. The experiments designed by RSM and the response data for every experimental condition is shown in Table 1.

Regression analysis has been done for fitting the responses. According to the software (Design Expert 8.0.1) (Stat-Ease, Inc., Minneapolis, USA), as the ratio of maximum value of response (94.3) to minimum value of response (41.0) is 2.3, much below the value 10, no transformation is required. Quadratic process order has been chosen after analysis of the data. The final equation (Eq. (7)) obtained after regression can be represented by corresponding coded factors as follows:

$$\begin{aligned} R_1 = 80.19 &+ 12.19^* A_1 + 7.04^* B_1 - 2.00^* C_1 \\ &+ 1.75^* D_1 + 1.03^* A_1^* C_1 - 1.23^* B_1^* C_1 - 3.28^* A_1^2 \\ &- 1.09^* B_1^2 - 1.61^* C_1^2 \end{aligned} \tag{7}$$

where

R_1 = Percentage removal of phenol (%), A_1 = Initial concentration of phenol, (mg/L), B_1 = Weight of shale, (g), C_1 = pH of solution during removal of phenol, D_1 = Temperature, (°C).

ANOVA reveals that all these four parameters show significant effect on phenol removal using Gondwana shale. Moreover, the quadratic effect of ini-

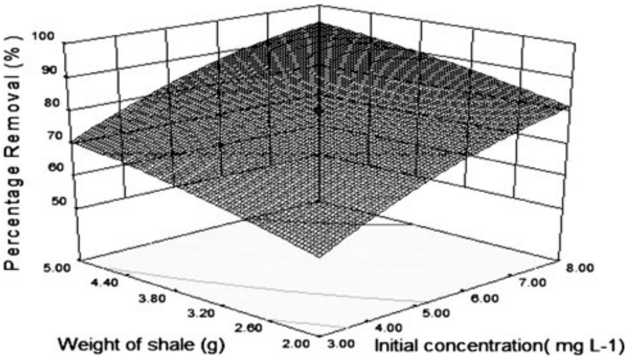

Fig. 5. Three dimensional response surface of the combined effect of initial concentration of phenol and weight of shale on the percentage removal of phenol.

tial concentration, amount of shale and pH of solution and the conjugate effect of amount of shale and pH have been found to be important.

The combined effect of initial concentration of phenol and amount of shale on the adsorption of phenol (C_1 = 7 and D_1 = 30°C) as shown in Fig. 5 vividly expresses that percentage removal of phenol from treated wastewater increases significantly with increase in either weight of adsorbent or initial concentration of phenol solution or both. Increase in weight of adsorbent leads to the increase in total surface area required for adsorption and thereby percentage removal of phenol has been increased. The higher percentage removal of phenol at higher initial concentration may be due to the higher mass transfer driving force provided the mass transfer process is controlled by diffusion rate. This observation has already been established from the analysis of kinetic data which reveals that kinetics of adsorption of phenol follows Morris Weber model indicating intraparticle diffusion rate controlled process.

Fig. 6 shows the three-dimensional response surface of the interactive effect of pH and initial concentration of phenol (B_1 = 3.5 g and D_1 = 30°C). Fig. 6 demonstrates that initial concentration of phenol has profound direct effect on the percentage removal of phenol at a fixed pH, which is already observed in Fig. 5. It is also seen from Fig. 6 that pH of solution has negligible effect on the percentage removal of phenol when initial concentration has been kept constant. It is a common fact that pH affects the ionization and protonation of compounds, which are influential factors in adsorption process [36]. The independent behavior of pH on percentage removal may be credited to the superior character of the adsorbent.

The conjugate effect of initial concentration of phenol and temperature of the solution has been demonstrated in Fig. 7 (B_1 =3.5 g and C_1 = 7). The effect of temperature on percentage removal of phenol is profound and direct when initial phenol concentration is less, whereas at higher initial concentration of phenol, temperature has negligible effect on percentage removal. At initial concentration of 3 mg/L, the percentage removal of phenol increased from 62 to 87% with corresponding increase in temperature from 25 to 35°C. On the other hand, removal is almost constant at 90%, when temperature was changed from 25 to 35°C at 8 mg/L initial phenol concentration. Mass flux of any solute is the product of mass transfer coefficient and the mass transfer driving force. Mass flux at low initial concentration of phenol (3 mg/L) largely depends on mass transfer coefficients, which is temperature sensitive. Thus, when temperature increases, mass transfer coefficient increases and thereby mass flux vis-à-vis rate of mass transfer increases as observed in the figure. Whereas at higher initial concentration of phenol solution, mass transfer driving force is so large that it governs the total mass transfer process and the increase in mass transfer coefficient due to increase in temperature has negligible effect on the overall mass transfer process.

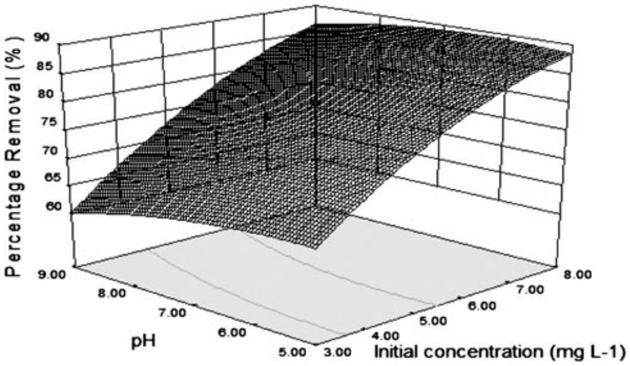

Fig. 6. Three dimensional response surface of the combined effect of initial concentration of phenol and pH on the percentage removal of phenol.

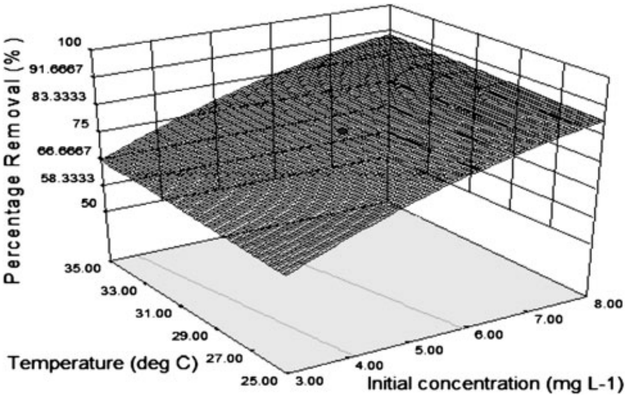

Fig. 7. Three dimensional response surface of the combined effect of temperature and initial concentration of phenol on the percentage removal of phenol.

Predicted values are obtained by solving the model equation at particular input condition, whereas actual values are obtained experimentally as response to that input condition. R^2, adjusted R^2 (R^2_{adj}), and predicted R^2 (R^2_{pred}) have been found to be 0.9837, 0.9685, and 0.9062, respectively. The reasons behind the rational values of these regressional coefficients are due to the choice of various input parameters in broad spectrum. The optimum condition for phenol removal is assessed by Design Expert Software by keeping pH and temperature constant at 9 and 30°C, respectively. The software has diagnosed the optimized condition as initial concentration of phenol: 8 mg/L, amount of shale: 2 g, pH: 9 and temperature: 30°C. Predicted per-

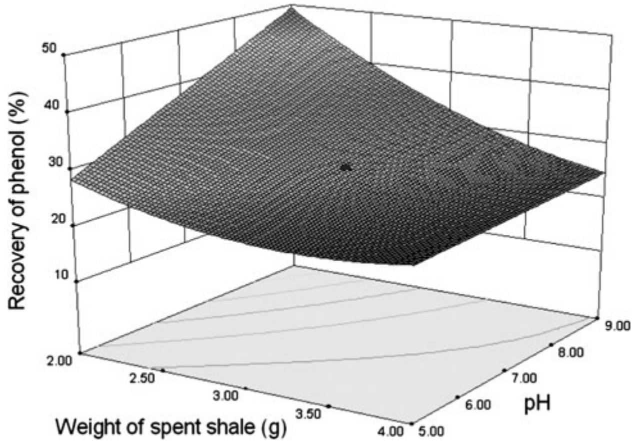

Fig. 8. Three dimensional response surface of the combined effect of weight of spent shale and pH on the percentage recovery of phenol.

centage removal of phenol (90.62) at the said condition matches satisfactorily well with the observations made with industrial wastewater (88.3%).

3.2.4. Recovery of phenol from treated industrial wastewater and its optimization

Three parameters, such as weight of spent shale, pH, and time, are taken into consideration as numeric factors, while the recovery of phenol is taken as response. The experimental design as done using RSM and the corresponding response data for every experimental condition is shown in Table 4.

Table 4
Experimental design for recovery of phenol

Sl. no.	Weight of spent shale (A_2, g)	pH (B_2)	Time (C_2, h)	Recovery of phenol (R_2, %)
1	4.00	5.00	36.00	25.33
2	3.00	10.36	30.00	35.33
3	3.00	3.64	30.00	20.00
4	2.00	5.00	36.00	27.67
5	2.00	9.00	36.00	50.67
6	3.00	7.00	30.00	28.00
7	2.00	5.00	24.00	23.33
8	3.00	7.00	30.00	28.00
9	4.00	9.00	36.00	27.33
10	1.32	7.00	30.00	53.33
11	4.00	5.00	24.00	21.33
12	3.00	7.00	30.00	28.00
13	4.00	9.00	24.00	24.67
14	3.00	7.00	19.91	18.00
15	4.68	7.00	30.00	21.62
16	3.00	7.00	30.00	28.00
17	3.00	7.00	30.00	28.00
18	3.00	7.00	30.00	28.00
19	2.00	9	30.00	44.67
20	3.00	7.00	40.09	30.33

Regression analysis has been done for fitting the responses by the Design Expert (8.0.1) software and quadratic process order has been chosen. The final equation (Eq. (8)) obtained can be represented by corresponding coded factors as follows:

$$\begin{aligned} R_2 = {} & +27.98 - 7.40^*A_2 + 5.53^*B_2 + 2.76^*C_2 \\ & - 4.87^*A_2^*B_2 - 0.46^*A_2^*C_2 + 0.040^*B_2^*C_2 \\ & + 3.51^*A_2^2 + 0.040^*B_2^2 - 1.20^*C_2^2 \end{aligned} \tag{8}$$

where A_2 = Weight of spent shale, (g), B_2 = pH of solution during recovery of phenol from spent shale, C_2 = Contact time, (h), R_2= Percentage recovery of phenol (%).

ANOVA reveals that all three parameters viz., weight of spent shale, pH, and contact time, show significant effect on percentage recovery of phenol. Contact time has profound effect on recovery of phenol which may be attributed to the fact that higher contact time ensures shale to spend higher time in solution thereby more amount of phenol may be desorbed to solution unless equilibrium is reached. Moreover, the conjugate effect of weight of spent shale and pH has been found to be significant.

Fig. 8 shows the three-dimensional response surface of the interactive effect of pH and weight of spent shale (C_2 = 36 h). Fig. 8 shows that with increase in weight of spent shale, there is a decrease in percentage recovery. Recovery of phenol is decreased from 50.67 to 27.33% and 27.33 to 25.33%, when weight of spent shale is increased from 2 to 4 g at pH 9 and 5, respectively. The reason behind this may be as follows: more amount of spent shale is associated with more amount of adsorbed phenol. If this phenol is desorbed, as volume of solution is constant (350 ml), the bulk concentration of phenol will be increased. thereby the mass transfer driving force as expressed by the difference between the concentration of phenol at surface of shale and the bulk concentration in solution will be decreased. Finally, the rate as well as the amount of desorption will be decreased. Thus, lower amount of shale is preferable in comparison with higher amount when recovery is concerned. Fig. 8 also shows that with increase in pH, there is an increase in percentage recovery of phenol. Recovery of phenol is increased from 27.33 to 50.67% and 25.33 to 27.33%, when pH is increased from 5 to 9 keeping weight of shale

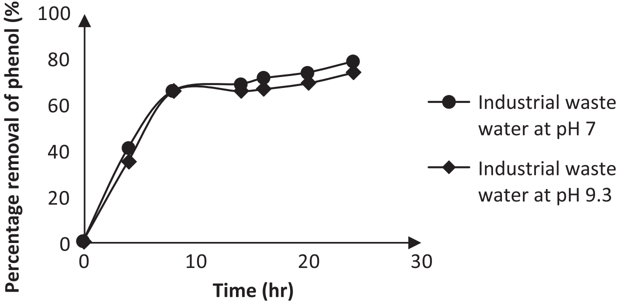

Fig. 9. Time series of percentage removal of phenol with untreated industrial wastewater at different pH conditions.

constant 2 and 4 g, respectively. Thus, it can be said that effect of pH is more pronounced at lower amount of shale.

R^2, Adjusted R^2 (R_{adj}) and predicted R^2 (R_{pred}) values have been found to be 0.9656, 0.9346 and 0.7374, respectively. The reasons behind the rational values of these regressional coefficients are due to the choice of various input parameters in broad spectrum. The software has diagnosed the optimized condition as weight of spent shale: 2 g, pH: 9 and contact time: 24 h. Predicted percentage recovery of phenol (44.86) at the said condition matches satisfactorily well with the observations made with industrial wastewater (44.67).

3.2.5. *Removal of phenol from untreated industrial wastewater by Gondwana shale*

The physicochemical properties of untreated wastewater collected directly from coke-oven battery of the same coke-oven plant has been determined. The untreated industrial wastewater has been characterized as color: brown, odor: obnoxious, pH: 9.3, COD: 2,400 mg/L, ammoniacal nitrogen: 1,700 mg/L and phenol: 400–476.24 mg/L. To examine the effectiveness of Gondwana shale in treatment of wastewater containing large amount of phenol, untreated wastewater has been contacted with shale at two different pH conditions viz., original wastewater having pH 9.3 and wastewater at pH 7. Fig. 9 shows the percentage removal-time series for the adsorption of phenol from raw industrial wastewater by Gondwana shale at these two pH conditions. From the figure, it is seen that pH has negligible effect on the removal efficacy of shale, and 74.11 and 78.79% removal have been obtained after 24 h when industrial wastewater was contacted with shale at pH 9.3 and pH 7 respectively, thereby the effectiveness of Gondwana shale in treatment of phenol laden waste is established both at lower and higher concentrations.

4. Conclusion

The phenol concentration in coke-oven plant effluent collected from industrial outfall lies in the range of 2–10 mg/L which is far beyond the standard limit of phenol emission and Gondwana shale, a noble, nonconventional abundantly available mine waste has been prescribed for its treatment. A thorough investigation is made by treating effluent with shale considering initial concentration of effluent, amount of shale, size of shale, and pH as process input parameters in a batch contactor. Results show that shale can be considered as good sorbent to remove phenol from wastewater. The percentage removal of phenol has been seen as high as 99.9%, when 2 g shale has been contacted with 100 ml of 6 mg/L phenol solution at pH 9. It is also seen that adsorption of phenol on Gondwana shale increases both with the increase in initial concentration of phenol and with weight of the adsorbent. The equilibrium data fit more satisfactorily to Langmuir model. RSM is employed to optimize the operating condition for removal of phenol. The shale obtained by removing phenol at optimum condition is used for recovery study to test its reusability. Recovery study shows that maximum 53.33% recovery is obtained when 1.32 g spent shale is contacted with 350 ml distilled water at pH 7 for 30 h. Furthermore, Gondwana shale is equally efficient to treat industrial wastewater containing phenol in much higher concentration collected directly from coke-oven battery. Thus, it can be stated that Gondwana shale, due to its unique physicochemical and mineralogical properties, can be used for the removal of phenol outside the laboratory condition with confidence.

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