



# Sorption studies of 4-NP onto goethite: effects of contact time, pH, concentration, ionic strength and temperature

Devsh Bhatt<sup>1</sup> · Namrata Gururani<sup>1</sup> · Anjana Srivastava<sup>1</sup> · Prakash Chandra Srivastava<sup>2</sup>

Received: 23 April 2020 / Accepted: 9 March 2021 / Published online: 25 March 2021  
© The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2021

## Abstract

The effects of different state variables (contact time, pH, concentration, ionic strength and temperature) were investigated on the adsorption of 4-nitrophenol (4-NP) onto goethite for its potential utilization in mitigating water pollution. The results suggested that the adsorption of 4-NP reached a quasi-steady state equilibrium at 24 h and followed pseudo-second order kinetics. The computed value of pseudo-second order rate coefficient for adsorption of 4-NP on goethite was  $447.57 \text{ kg mM}^{-1} \text{ h}^{-1}$ . Adsorption of 4-NP on goethite was higher when the solution pH was  $< \text{pH}_{\text{zpc}}$  of goethite and near  $\text{pK}_a(7.15)$  of 4-NP and vice versa. The effect of concentration of 4-NP on adsorption revealed the heterogeneity of sorption sites on goethite surface; highly selective sites of higher bonding energy up to sorption density of  $1.42 \text{ mM kg}^{-1}$  and lower selectivity sites of lesser bonding energy for sorption density above  $2.07 \text{ mM kg}^{-1}$ . An increase in ionic strength, increased the adsorption of 4-NP on goethite but an increase in temperature decreased the adsorption. The changes in thermodynamic parameters indicated that adsorption of 4-NP was a spontaneous and exothermic reaction with an increase in the entropy of the system. Based on these results, the optimal conditions for the maximal removal of 4-NP were 6.7–7.0 pH, 0.015–0.02 ionic strength, 15 °C temperature with 1: 100 goethite (sorbent)-solution ratio.

**Keywords** Sorption · Goethite · 4-Nitrophenol · Kinetics · Variables

## Introduction

Nitrophenols are among the most important and versatile industrial organic compounds which are widely used as raw materials or intermediates in the manufacture of explosives, pharmaceuticals, pesticides, pigments, dyes, wood preservatives and rubber chemicals (Qui et al. 2007). The wastes generated from these industries often find way to water reservoirs leading to contamination of water resources. The United States Environmental Protection Agency (USEPA) has listed 2-nitrophenol, 4-nitrophenol, and 2, 4-dinitrophenol as priority pollutants (USEPA 1980) and set the tolerance limit for total phenolic compounds in drinking water

as  $0.001 \text{ mg L}^{-1}$  (IS 2012). The USEPA has also set pre-treatment standards for waste discharge from manufacturing industries to avoid the subsequent damage caused by 4-nitrophenol (4-NP) to aquatic environment. Unfortunately, an efficient removal of 4-NP is still a challenge because of its high solubility and stability in water as well as its resistance to the conventional water purification methods (Marais and Nyokong 2008). Different techniques such as membrane filtration (Ivančev-Tumbass et al. 2008), degradation (Chen et al. 2011; Xiong et al. 2012) adsorption (Ivančev-Tumbass et al. 2008; Mehrizad et al. 2012; Yuan-Xiang et al. 2014; Varank et al. 2012) and chemical reduction (Qiu et al. 2012; Jin et al. 2012; Fan et al. 2012) have been suggested for the removal of nitrophenol from contaminated waters but most of these divulged methods suffer from disadvantages such as high capital investment and large operative costs (Lin and Hsieh 2015; Polat et al. 2006). However, the adsorption technique appears to be a globally accepted and low cost method for the removal of phenols from water due to its placid application as well as low initial cost (Juny et al. 2001; Ramirez et al. 2017). It can therefore, be useful to develop a low cost and efficient method for elimination of 4-NP from waters.

✉ Anjana Srivastava  
anj612003@gmail.com

<sup>1</sup> Department of Chemistry, College of Basic Sciences and Humanities, G. B. Pant University of Agriculture and Technology, Pantnagar, Uttarakhand 263145, India

<sup>2</sup> Department of Soil Science, College of Agriculture, G. B. Pant University of Agriculture and Technology, Pantnagar, Uttarakhand 263145, India

In recent years, different natural mineral and organic materials such as zeolite (Pham et al. 2016), alumina (Aazza et al. 2017), montmorillonite (Ouardi et al. 2019), Mansonia sawdust (Ofomaja and Unuabonah 2013), and Brazilian peat (Jaerger et al. 2015) have been tried as alternative adsorbents in the treatment of phenolic contaminated waste water.

Goethite [ $\alpha$ -FeO(OH)], a thermodynamically stable iron oxyhydroxide, is a widespread mineral (Cornell and Schwertmann 2003) having closely packed oxygen and hydroxyl anions in hexagonal arrangement with iron cations in octahedra. The crystal structure of goethite has interface stereochemistry of the type [(H<sub>2</sub>O)-(H<sub>2</sub>O)-OH<sub>2</sub>-OH-Fe-O-O-Fe-R]. This indicates the presence of two layers of adsorbed water, a hydroxo- group and an aquo- group (Ghose et al. 2010). These physicochemical properties of goethite impart it a great potential as an adsorbent due to its special surface active sites and large surface area. Goethite is usually formed in lithosphere through weathering of iron-rich minerals and is a common soil mineral. It is also known to be present in groundwater as precipitant mineral (Liu et al. 2014). The mineral has high adsorption capacity for anions, organic acids and cations in the natural environment and has prospective application in environmental preservation (Tejedor et al. 1992). Since the adsorption of organic compounds such as phenols on goethite depends upon the pH and composition of cations in solution, concentration of soluble organics and ionic strength of solution etc. (Tran et al. 1999), therefore, it is very important to study the effect of different state variables on adsorption of 4-NP onto goethite which may help in developing a protocol for effective removal of 4-NP using goethite. The present study was undertaken to investigate the effects of contact time, pH, ionic strength, temperature on adsorption–desorption behavior of 4-nitrophenol on goethite.

## Experimental section

Goethite [ $\alpha$ -FeO(OH)] was synthesized in the laboratory by taking 250 mL of 0.5 M solution of iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9 H<sub>2</sub>O, AR grade) prepared in CO<sub>2</sub> free water and slowly neutralizing this solution by gradual addition (2 mL/min.) of CO<sub>2</sub> free solution of 0.7 M KOH. The precipitated ferric hydride was aged at room temperature (27 °C) at pH 12 for 2 days followed another aging in water bath at 60 °C for next 2 days (Atkinson et al. 1968). The soluble impurities were removed by repeated washing with deionised water. All chemicals used in the study were of analytical grade procured from SD Fine Chemicals, Mumbai. Double distilled water used in the study was prepared using Quartz double distillation unit (Borosil, Mumbai).

## Study on effect of contact time

Two hundred mg of goethite sample was taken in twenty centrifuge tubes and 0.2 mL of 1 M KCl and 1 mL of a stock solution of 4-NP (40 mgL<sup>-1</sup>) were added to each tube. The volume of the solutions in the tubes was made up to 20 mL by adding double distilled water. Thereafter, the suspensions were shaken in a shaker incubator at 120 rpm for different time intervals (0, 0.5, 1, 2, 4, 6, 12, 24, 48 and 72 h). The centrifuge tubes were removed in duplicate after each time interval and centrifuged at 7000 rpm for 10 min. Supernatant was collected and divided into two portions. One portion was used for recording the pH and the other portion was passed through 0.45 µm filter paper for quantitative estimation by high performance liquid chromatography. Since the quasi-steady equilibrium for adsorption of 4-NP onto goethite was found to be 24 h, it was uniformly adopted in the subsequent studies on effect of other state variables. The adsorbed amount of 4-NP onto goethite was calculated as:

$$Q_t = \frac{(C_0 - C_t)}{w} \times V_{sol}$$

where  $Q_t$  is adsorbed amount of 4-NP in mM kg<sup>-1</sup> at time ( $t$ ),  $C_0$  and  $C_t$  are the initial and final concentration of 4-NP in mM L<sup>-1</sup>,  $w$  is weight of goethite (0.2 g) and  $V_{sol}$  is volume of solution (20 mL). Desorption of 4-NP adsorbed by goethite at different time intervals was also carried out by resuspending the centrifuged goethite pellet into 19.8 mL of water + 0.2 mL of 1 M KCl and shaking the contents in shaker incubator at 120 rpm for 24 h. The contents were centrifuged at 7000 rpm for 10 min. The Supernatants were collected and determined for pH and concentration of 4-NP as described in the preceding paragraph. The remaining adsorbed amount of 4-NP after desorption was computed as:

Remaining adsorbed amount of 4-NP after desorption ( $Q$ ) = ( $Q_t - (C_{des.} \times V_{sol})$ )/ $w$

Where,  $Q_t$  is adsorbed amount of 4-NP in mM kg<sup>-1</sup> at time ( $t$ ),  $C_{des.}$  desorbed concentration of 4-NP in mM L<sup>-1</sup>,  $w$  is weight of goethite (0.2 g) and  $V_{sol}$  is volume of solution (20 mL).

## Study on effect of equilibrium pH

Two hundred mg goethite was taken in twenty centrifuge tubes. To each tube 0.2 mL of 1 M KCl and 1 mL stock solution of 4-NP (40 mgL<sup>-1</sup>) were added. Different volumes (1, 2, 3 and 4 mL) of 0.01 M HCl and (1, 2, 3, 4 and 5 mL) 0.01 M KOH were added separately to the respective tubes in duplicate. The volume of solutions was made up to 20 mL in all the tubes by adding double distilled water. The suspensions were shaken for 24 h in a shaker incubator at 120 rpm,

the suspensions were centrifuged at 7000 rpm for 10 min. Clear supernatant was collected for recording the pH and quantitative analysis of 4-NP as mentioned in the preceding section. To study desorption behavior, goethite pellet in each tube was re-dispersed in 0.2 mL of 1 M KCl and different volumes of 0.01 M HCl and KOH (as mentioned above) were added and the final volume in all tubes was made up to 20 mL by addition of double distilled water. The suspensions were equilibrated for 24 h followed by centrifugation at 7000 rpm for 10 min. Clear supernatant was collected and analyzed as mentioned in preceding section. The adsorbed amount of 4-NP by goethite and the remaining adsorbed amount of 4-NP after desorption were calculated as described in the preceding section.

### Study on effect of sorbate concentration

To examine the effect of concentration on adsorption of 4-NP, 200 mg of goethite was taken in twelve centrifuge tubes. An aliquot of 0.2 mL of 1 M KCl and different volumes (0.25, 0.50, 1.0, 1.5, 2.0 and 2.5 mL) of 4-NP stock solution ( $40 \text{ mg L}^{-1}$ ) were added to these tubes and the final volume was made to 20 mL in all tubes by adding requisite volume of double distilled water. The contents were equilibrated in a shaker incubator for 24 h at 120 rpm. After equilibration, the contents were centrifuged at 7000 rpm for 10 min. Clear supernatants were collected for recording the equilibrium pH and HPLC analysis. For desorption study, 0.2 mL 1 M KCl was added to the goethite pellet retained in centrifuge tubes after the removal of supernatant and the volume was made up to 20 mL by addition of double distilled water. Suspensions were equilibrated for 24 h at 120 rpm followed by centrifugation at 7000 rpm for 10 min. The supernatant was collected and analyzed as for adsorption experiment. The adsorbed amount of 4-NP by goethite and the remaining adsorbed amount of 4-NP after desorption were calculated as described in the preceding section.

### Study on effect of ionic strength

Two hundred mg goethite was taken in eight centrifuge tubes. One mL of stock solution of 4-NP ( $40 \text{ mg L}^{-1}$ ) and different volumes (0, 0.2, 0.3 and 0.4 mL) of 1 M KCl were added separately to centrifuge tubes in duplicate and final volume was maintained to 20 mL by adding requisite amount of double distilled water so as to get the final ionic strength of 0, 0.01, 0.015 and 0.02. The contents were equilibrated for 24 h in a shaker incubator at 120 rpm. After equilibration, the contents were centrifuged at 7000 rpm for 10 min. Clear supernatant was collected to record equilibrium pH and for estimation of 4-NP. Desorption experiment was also done at different ionic strengths as stated above. The adsorbed amount of 4-NP by goethite

and the remaining adsorbed amount of 4-NP after desorption were calculated as described in the preceding section.

### Study on effect of temperature

Two hundred mg goethite was taken in six centrifuge tubes. Then, 0.2 mL of 1 M KCl and 1 mL of stock solution of 4-NP ( $40 \text{ mg L}^{-1}$ ) were added to these tubes. The final volume was made up to 20 mL by adding double distilled water and the suspensions were shaken for 24 h in a shaker incubator at three different temperatures (15, 25 and 35 °C) in duplicate. After equilibration, the contents were centrifuged at 7000 rpm for 10 min. The clear supernatants were collected for recording the pH and for estimation of 4-NP. Desorption experiment was also done at different temperatures as stated above. The adsorbed amount of 4-NP by goethite and the remaining adsorbed amount of 4-NP after desorption were calculated as described in the preceding section.

The data on adsorption of 4-NP onto goethite surface at varying temperatures were also used to calculate the thermodynamic equilibrium constant for adsorption onto goethite surface considering the dissociated species of 4-NP at equilibrium pH (7.79 to 8.23) using the expression indicated below:

$$K^0 = (\text{Adsorbed 4-NP}) / (a_{4\text{-NP}} / a_{\text{OH}^-})$$

Free energy change ( $\Delta G_r$  in  $\text{kJ mol}^{-1}$ ) was calculated as  $\Delta G_r = -RT \ln K^0$  where, R and T are gas constants and temperature in Kelvin. Enthalpy ( $\Delta H_r$  in  $\text{kJ mol}^{-1}$ ) and entropy ( $\Delta S_r$  in  $\text{kJ mol}^{-1} \text{ degree}^{-1}$ ) were calculated as the intercept and slope of a plot drawn between  $\Delta G_r$  and temperature (T in Kelvin).

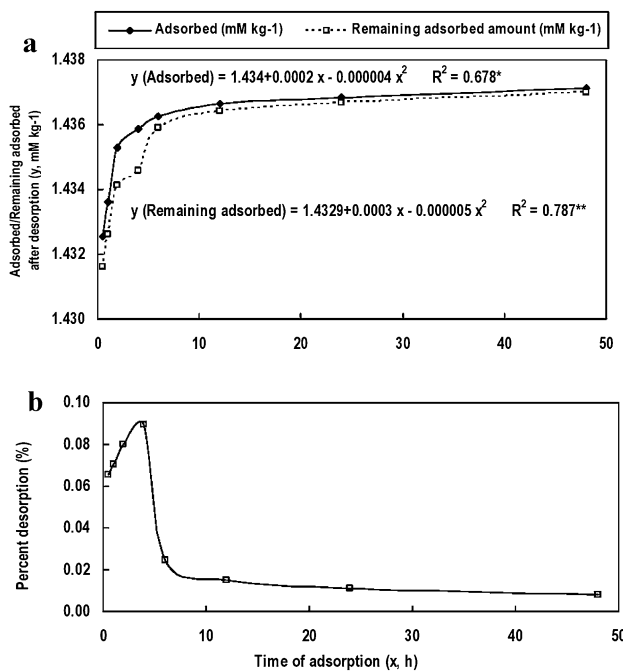
### Quantitative estimation of 4-NP

The quantitative estimation of 4-NP was done using high performance liquid chromatography (Ultimate 3000 HPLC, Dionex, USA) equipped with C18 column, ( $250 \times 4.6 \text{ mm i.d.}, 5 \mu\text{m}$ ) under isocratic mode, with methanol and water (v/v) in a ratio of 80:20 as a mobile phase at a flow rate of  $1 \text{ mL min}^{-1}$  and UV detection at 310 nm. The retention time of 4-NP was 3.413 min under the above conditions. The limit of detection (LOD) and limit of quantification (LOQ) were determined on the basis of S/N ratio for 4-NP and were found to be 0.004 and  $0.009 \mu\text{g g}^{-1}$ , respectively.

## Results and discussion

### Effect of contact time

Adsorption of 4-NP onto goethite increased gradually reaching a quasi-steady state equilibrium at 24 h of equilibration and adsorption efficiency of goethite to remove 4-NP from aqueous solution at 24 h was found to be 99.94 percent. Beyond 24 h, further increase in adsorption was only minimal (Fig. 1). The equilibrium time for 4-NP adsorption onto nano zeolite (Pham et al. 2016) or montmorillonite (Ouardi et al. 2019) has been reported to range between 2 to 2.5 h and variations between earlier findings and the observations of the present investigation could be attributed to the differences in the nature of adsorbent used in the study and speed of the shaker. The desorption data showed that the



**Fig. 1** Amount of 4-NP adsorbed onto goethite and the amount remaining adsorbed after desorption (a) and percent desorption (b) of 4-NP.  $R^2$  coefficient of determination, \*\* Significant at  $p \leq 0.01$ , \* Significant at  $p \leq 0.05$

reversibility of adsorbed 4-NP increased with increasing adsorption period up to 4 h from 0.06 to 0.09 percent due to the increase in adsorbed amount of 4-NP. However, beyond 4 h of equilibration period, the percent desorption decreased with increasing equilibration period. This also revealed that prolonged adsorption period beyond 4 h allowed the entry of adsorbed 4-NP to those sites from where the desorption of adsorbed 4-NP was relatively difficult. At 48 h of equilibration for adsorption, the percent desorption of 4-NP was only 0.008 percent.

### Kinetic models

Considering the excess availability of adsorption sites on the sorbent (goethite) which may not pose a limitation in the progress of sorption reaction, we opted to fit adsorption data of 4-NP on goethite at different time intervals to pseudo-first- and pseudo-second- order kinetics. Since the transformation of the kinetic equation to linear forms brings in significant problems in estimating kinetic parameters due to alterations in the error structure and normality of standard least square (Ho 2004; Gimbert et al. 2008), only non-linear pseudo-first- and pseudo-second- order equations were used to fit the kinetic data using my curve fit free software.

Pseudo - first order (non - linear form)  $Q_t = Q_e \cdot (1 - e^{-K_1 t})$  (1)

Pseudo second order (non - linear form)

$$Q_t = (Q_e^2 \cdot K_2 \cdot t) / (1 + Q_e \cdot k_2 \cdot t), \quad (2)$$

where  $Q_t$  and  $Q_e$  are the amount of 4-NP adsorbed ( $\text{mM kg}^{-1}$ ) at time ( $t$ ) and at the equilibrium, respectively. The  $k_1$  ( $\text{h}^{-1}$ ) and  $k_2$  ( $\text{kg mM}^{-1} \text{h}^{-1}$ ) are the rate coefficients for pseudo-first- and pseudo-second- order kinetics, respectively. As the inclusion of observations close to the equilibrium time may unduly favor the validity of pseudo-second order kinetics (Simonin 2016), the observation data at 48 h of equilibration was excluded from the kinetic modeling.

The computed values of kinetic parameters, coefficient of determination ( $R^2$ ) and standard error of estimate (S.E.) are presented in Table 1. Adsorption kinetics of 4-NP on goethite conformed best to pseudo-second

**Table 1** Computed values of kinetic parameters pertaining to non-linear pseudo-first and pseudo-second order models for adsorption of 4-NP onto Goethite

Kinetic model	$Q_{e \text{ exp}}$ ( $\text{mM kg}^{-1}$ )	$Q_{e \text{ pred.}} \pm \text{S.E}$ ( $\text{mM kg}^{-1}$ )	Rate constant ( $k \pm \text{S.E.}$ )	Coefficient of determination ( $R^2$ )	Standard error of estimate (S.E.)
Pseudo-first order	1.4371	$1.4357 \pm 0.0005$	$12.1841 \pm 0.7789 \text{ h}^{-1}$	0.568	0.0012
Pseudo-second order	1.4371	$1.4366 \pm 0.0002$	$447.57 \pm 48.72 \text{ kg mM}^{-1} \text{ h}^{-1}$	0.944**	0.0004

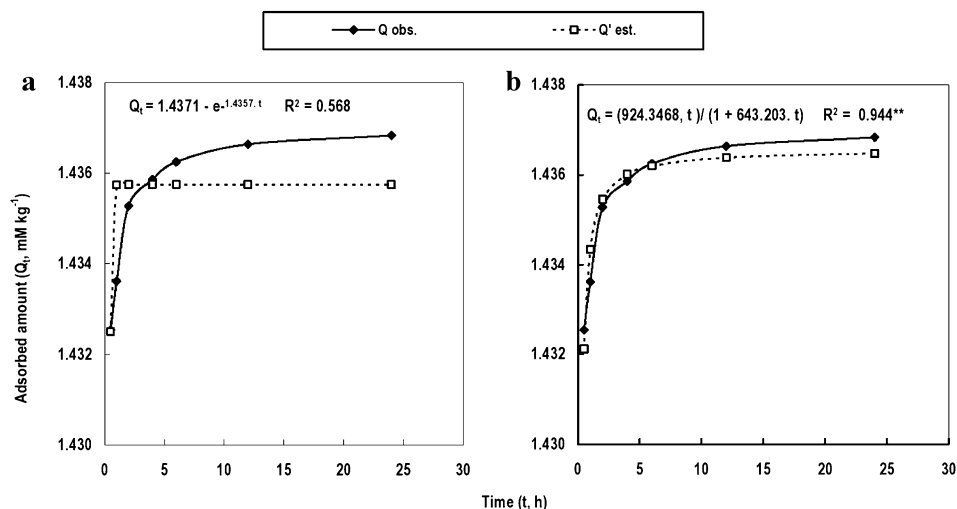
\*Significant at  $p \leq 0.05$  and \*\* significant at  $p \leq 0.01$

order kinetics, as with this model the value of  $R^2$  was higher while S.E. was lower as compared to pseudo-first order. The graphical representations of pseudo-first- and pseudo-second-order kinetic models are shown in Fig. 2. The rate coefficient for adsorption of 4-NP on goethite as per pseudo-second order kinetics was found to be  $447.57 \text{ kg mM}^{-1} \text{ h}^{-1}$ . Gladysz-Plaska (2017) also observed that phenol and phosphate anion adsorption on modified clay followed a pseudo-second order kinetics. Magdy et al. (2018) also reported that the experimental kinetic data on the removal of 2,4- dinitrophenol, 2 nitrophenol and 4 nitrophenol from aqueous solution by char ash obtained from animal bones fitted well to pseudo-second order model.

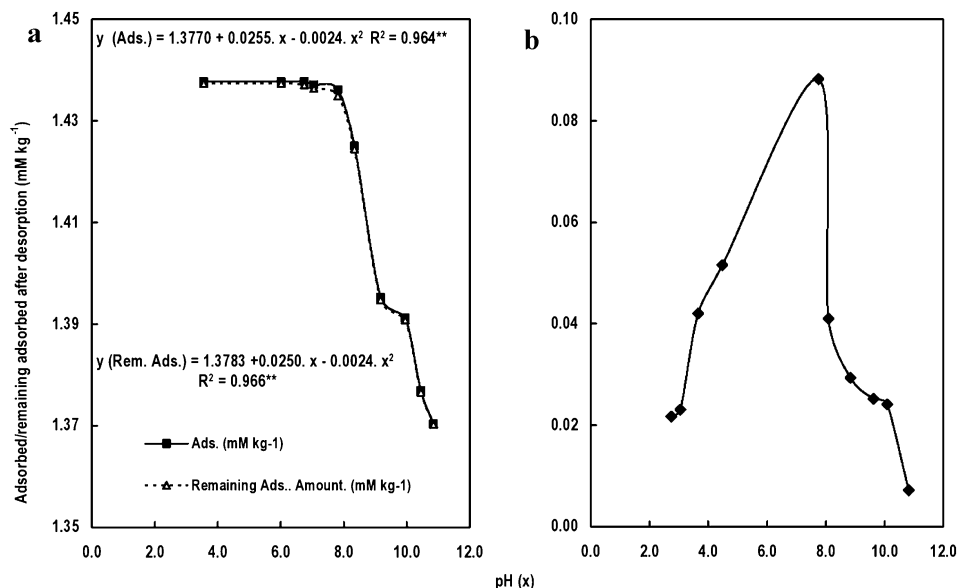
### Sorption of 4-NP on goethite as a function of equilibration pH

The amount of 4-NP adsorbed on goethite remained constant under acidic equilibrium pH i.e. from 3.55 to 6.75 but further increase in equilibrium pH decreased the adsorption (Fig. 3a). As shown in the Fig. 3a, the pH of the solution influenced the sorption of 4-NP via altering the surface charge on mineral and also influencing the dissociation of 4-NP. Hence, the magnitude by which equilibrium pH deviates from  $\text{pH}_{\text{zpc}}$  (pH for point of zero charge) of goethite could play a decisive influence on adsorption of 4-NP onto goethite. Iron oxides in general are reported to hold positive charge at  $\text{pH} < \text{pH}_{\text{zpc}}$ , and negative charge at  $\text{pH} > \text{pH}_{\text{zpc}}$  (Brown et al. 1999) and the  $\text{pH}_{\text{zpc}}$  of goethite was in the pH range of 7.0–7.5 (Cornell and Schwertmann 2003).

**Fig. 2** Psuedo-first (a) and Psuedo-second (b) order kinetic models fitted to adsorption of 4-NP onto goethite.  $Q_{\text{obs}}$  is observed adsorbed amount and  $Q'_{\text{pred}}$  is predicted adsorbed amount as per the kinetic model.  $R^2$  coefficient of determination, \*\* Significant at  $p \leq 0.01$



**Fig. 3** Effect of equilibrium pH on adsorption and desorption of 4-NP (a) onto goethite and percent desorption (b) of 4-NP.  $R^2$ : Coefficient of determination, \*\* Significant at  $p \leq 0.01$



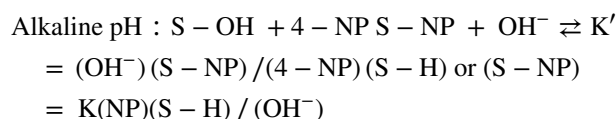
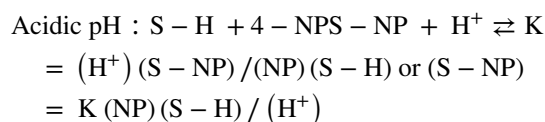
Consequently, with the pH of the solution less than 7, the adsorption of 4-NP on goethite was higher due to electrostatic attraction (H-bonding) of  $\text{NO}_2$  moiety on positively charged surface of goethite. The decrease in adsorption of 4-NP in alkaline pH could be ascribed to the fact that at alkaline pH, a net negative charge was likely to develop on the goethite surface and 4-NP also got dissociated into an anion ( $\text{p}K_a$  7.15) which might have caused an electrostatic repulsion between the negatively charged reactive surface sites of goethite and the anionic 4-NP species. However, at pH above  $\text{p}K_a$  of 4-NP, sorption of 4-NP anion ( $4\text{-NP}^-$ ) was effected due to bonding between surface  $\text{Fe}^{3+}$  and phenolate anion. McBride and Kung (1991) presented Fourier transformed infra-red spectral evidence to reveal the bonding between surface  $\text{Fe}^{3+}$  and phenolic ligand of substituted phenols and concluded that depending upon the level of adsorption, both physically and chemically adsorbed phenols could be detected on goethite and amorphous Fe oxide. Thus, the maximum adsorption of 4-NP on goethite could occur till the pH of the system was below the  $\text{p}K_a$  of 4-NP. Al-Ahmari et al. (2018) also recorded the maximum adsorption of 4-n-nonyl phenol on goethite at equilibrium pH close to  $\text{p}K_a$  of this phenolic compound. There was a significant quadratic relationship between the equilibrium pH and adsorbed amount of 4-NP onto goethite or the amount remaining adsorbed after desorption; both relationships were significant at  $p \leq 0.01$ .

A strong pH dependence of the percent desorption was also observed in the pH region which corresponded to the

$\text{p}K_a$  of 4-NP. Desorption of 4-NP carried out on the adsorption samples showed an increasing percent desorption from equilibrium pH of 2.75 to 7.75. The maximum percent desorption was observed to be 0.088 percent at equilibrium pH of 7.75 (Fig. 3b). Above equilibrium pH 7.75, a persistent decrease in percent desorption was observed reaching to the level of 0.007 percent at pH 10.82 due to decrease in adsorption of dissociated 4-NP anion.

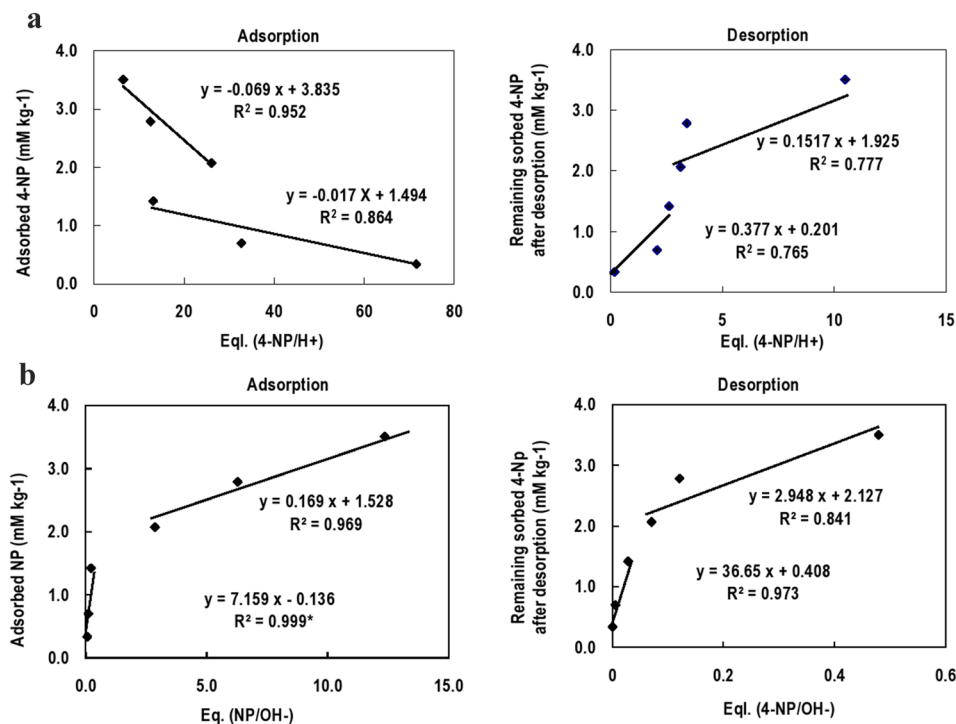
### Effect of concentration

The interaction of 4-NP with goethite surface can be anticipated by the following schematic equations:



The adsorbed amounts of 4-NP were plotted against the ratio of  $4\text{-NP}/\text{H}^+$  or  $4\text{-NP}/\text{OH}^-$  in equilibrium solution (Fig. 4). Since the equilibrium pH in this study for different concentration of 4-NP varied from 6.86 to 8.51, a plot of  $4\text{-NP}/\text{OH}^-$  better conformed to adsorption–desorption data

**Fig. 4** 4-NP/ $\text{H}^+$  model (a) and 4-NP/ $\text{OH}^-$  model (b) for adsorption and desorption of 4-NP.  $R^2$  coefficient of determination, \* Significant at  $p \leq 0.05$



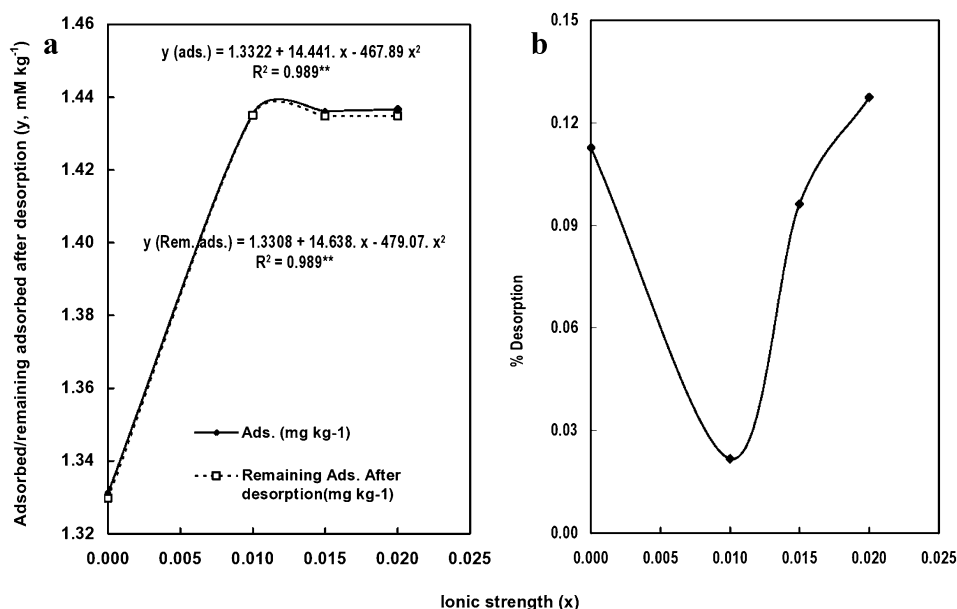
of 4-NP on goethite compared to 4-NP/H<sup>+</sup> as evident from higher values of coefficient of determination ( $R^2$ ). A close observation of the data revealed two subsections of varying slopes in 4-NP/OH<sup>-</sup> indicating heterogeneity of the goethite adsorption surface for 4-NP sorption wherein, the sites of higher and lower specificity were likely to exist in the system. As shown in Fig. 4, highly selective sorption sites of higher bonding energy for 4-NP existed up to a sorption density of 1.42 mM kg<sup>-1</sup> while the sites of relatively lower selectivity with lesser bonding energy occurred above the sorption density of 2.07 mM kg<sup>-1</sup>. The selectivity coefficients for 4-NP adsorption computed from NP/OH<sup>-</sup> plots were found to be 7.159 and 0.169 for high and low energy bonding sites, respectively. For desorption isotherms, the computed values of selectivity coefficients for desorption from higher and lower bonding sites were 36.651 and 2.948, respectively. The values of selectivity coefficient for desorption were many folds higher than selectivity coefficient for adsorption and this indicated a hysteretic effect in case of 4-NP adsorption onto goethite surface. Similar results were obtained in the adsorption study of phenol by bentonite (Banat et al. 2000). An increase in the initial 4-NP concentration increased the mass transfer driving force and therefore, the rate at which 4-NP molecules passed from the bulk solution to the particle surface was higher and this resulted in higher adsorption.

### Effect of ionic strength

An increase in adsorption of 4-NP on goethite was observed with increasing ionic strength (Fig. 5a). The maximum increase in adsorption was noted when ionic strength increased from 0 to 0.01 and thereafter, with further increase

in ionic strength up to 0.02 only a slight increase occurred in adsorption of 4-NP onto goethite. An increase in ionic strength is known to decrease the thickness of the diffused double layer around the colloidal surfaces (Sparks 1998) and could effectively bring more 4-NP molecules close to goethite surface to effect H-bonding of 4-NP molecules with the surface aquo- and hydroxyl- groups of goethite at higher ionic strengths. The desorption of 4-NP showed that with the increase in ionic strength from 0 to 0.01 there was a decrease in percent desorption from 0.113 to 0.022 percent. Further increase in the ionic strength up to 0.02 resulted an increase in percent desorption from 0.022 to 0.128% (Fig. 5b). The possible reason for the observed effect might be that the presence of extra salts could cause a salting-out effect. The dissociative ions in solution form well-organized ionic atmospheres through binding water molecule tightly which decreases the solubility of anion-electrolyte (i.e. 4-NP) in solution and consequently result in an increase in the adsorption of 4-NP (Cannata et al. 2011). On further increasing the ionic strength of solution to 0.02, the presence of salt might have blocked some active sites of goethite, so 4-NP molecules were hindered to combine with the sites of higher bonding energy onto goethite surface, therefore, only a slight increase in adsorption of 4-NP on goethite was observed and such retention of 4-NP onto goethite was reversible. Similar results were obtained by Wang et al. (2014) in an adsorption study of phenol over modified activated clay. The increase in adsorbed amount of 4-NP onto goethite with the increase in ionic strength closely could be successfully described by a quadratic equation and the relationship was found to be statistically significant at  $p \leq 0.01$ .

**Fig. 5** Effect of ionic strength on adsorption and desorption (a) of 4-NP on goethite and Percent desorption (b) of adsorbed 4-NP.  $R^2$  coefficient of determination, \*\* Significant at  $p \leq 0.01$



## Effect of temperature

A decrease in adsorption of 4-NP on goethite was observed with increasing temperature and this clearly indicated that adsorption of 4-NP was principally a physical adsorption (Fig. 6a). Desorption of 4-NP also increased with the increasing temperature (Fig. 6b). The adsorbed amount of 4-NP onto goethite as well as its percent desorption followed a close quadratic relationship with the temperature (significant at  $p \leq 0.01$ ). These observations clearly indicated that the bonding of 4-NP onto goethite surface was dominantly a physical phenomenon possibly due to weak electrostatic attractions or H-bonding. Senturk et al. (2009) also reported similar types of results while studying adsorption of phenol on an organo-bentonite.

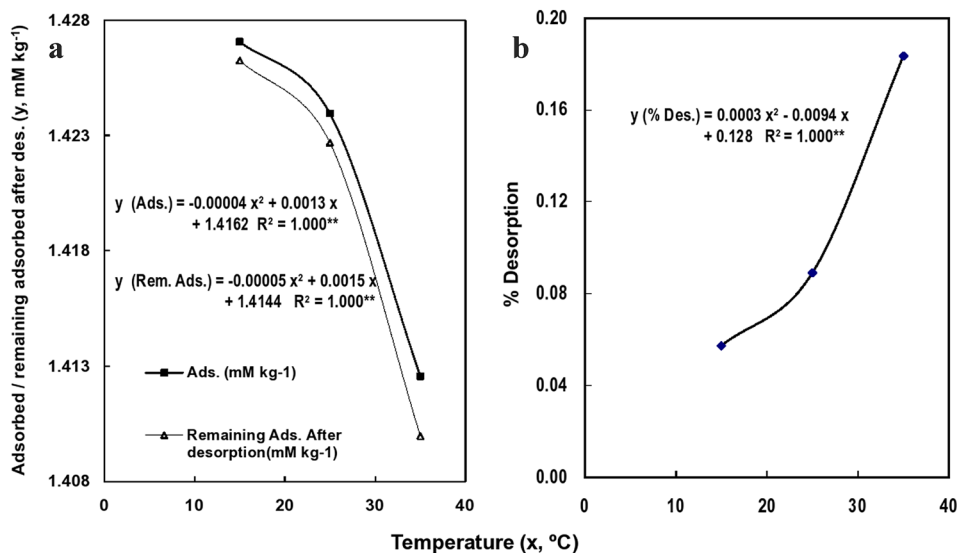
The data on thermodynamic equilibrium constant ( $K^0$ ), free energy- ( $\Delta G_r$ ), enthalpy- ( $\Delta H_r$ ) and entropy- ( $\Delta S_r$ ) change are presented in Table 2. A decrease in  $\Delta G_r$  and  $\Delta H_r$  in the adsorption reaction of 4-NP on goethite indicated that the adsorption of 4-NP was a spontaneous and exothermic reaction. As the value of enthalpy change was less than  $40 \text{ kJ mole}^{-1}$  the sorption of 4-NP by goethite appeared to be mainly a physical process. In a study on the removal of 4-NP from aqueous solution, Varank et al. (2012) also reported that adsorption of 4-NP onto zeolites and bentonite was a

spontaneous and exothermic process. A positive value of  $\Delta S_r$  indicated an increase in the randomness of the system due to H-bonding of 4-NP, dissociation of 4-NP induced by direct bonding between surface  $\text{Fe}^{+3}$  atoms of goethite and 4-NP anion and release of  $\text{OH}^-$  ions in exchange of 4-NP anion. Kung and McBride (1991) also noted that the deprotonation of monochlorophenol on goethite surface was induced by the direct bonding between surface Fe atoms and phenolate anion.

## Conclusions and recommendations

Equilibration time for adsorption of 4-NP on goethite was 24 h which followed pseudo-second order kinetics. The equilibrium pH of the solution of 4-NP and  $\text{pH}_{zpc}$  of goethite controls the sorption of 4-NP onto goethite. Adsorption – desorption isotherms of 4-NP were closely related to 4-NP/ $\text{OH}^-$  ratio indicating the exchange of  $\text{OH}^-$  from goethite surface with 4-NP adsorption. An increase in ionic strength favored sorption of 4-NP onto goethite. Adsorption of 4-NP under varying temperatures indicated that adsorption of 4-NP onto goethite surface was dominantly physical. Due to special physicochemical properties like surface density and specific structure goethite mineral can

**Fig. 6** Effect of temperature on adsorption–desorption of 4-nitrophenol onto goethite (a) and percent desorption (b) of 4-NP.  $R^2$  coefficient of determination, \*\* Significant at  $p \leq 0.01$



**Table 2** Thermodynamic equilibrium constant ( $K$ ), changes in Gibb's free energy ( $\Delta G_r$ ), enthalpy ( $\Delta H_r$ ) and entropy ( $\Delta S_r$ ) for 4-NP onto Goethite

Soil series	Temp. ( $^{\circ}\text{C}$ )	Thermodynamic Eq. constant ( $K$ )	$\Delta G_r$ ( $\text{kJ mol}^{-1}$ )	$\Delta H_r$ ( $\text{kJ mol}^{-1}$ )	$\Delta S_r$ ( $\text{kJ mol}^{-1} \text{ deg}^{-1}$ )
Goethite	15	2.134512	- 1.816		
	25	1.646479	- 1.235	- 32.160	0.105
	35	0.892612	0.281		



be recommended for removal of the priority pollutant 4-NP, a commonly found contaminant, in wastewaters released from industries. According to the results of present investigation, the optimal conditions for the maximal removal of 4-NP were 6.7–7.0 pH, 0.015–0.02 ionic strength, 15 °C temperature with 1: 100 goethite (sorberent)-solution ratio. However, more studies need to be undertaken for confirming the removal of other priority organic pollutants from wastewaters using goethite as an adsorbent.

**Funding** No specific funds were granted for undertaking the study.

## Declarations

**Conflict of interest** The authors declare no conflict of interest.

## References

- Aazza M, Ahlafi H, Moussout H, Maghat H (2017) Ortho-nitro-phenol adsorption onto alumina and surfactant modified alumina: kinetic, isotherm and mechanism. *J Environ Chem Eng* 5:3418–3428. <https://doi.org/10.1016/j.jece.2017.06.051>
- Al-Ahmari SD, Watson K, Fong BN, Ruyonga RM, Ali H (2018) Adsorption kinetics of 4-n- Nonyl phenol on hematite and goethite. *J Environ Chem Eng* 6(4):4030–4036. <https://doi.org/10.1016/j.jece.2018.05.052>
- Atkinson RJ, Posner AM, Quirk JP (1968) Crystal nucleation in Fe(III) solutions and hydroxide gels. *J Inorg Nucl Chem* 30(9):2375–2381. [https://doi.org/10.1016/0022-1902\(68\)80247-7](https://doi.org/10.1016/0022-1902(68)80247-7)
- Banat FA, Al-Bashir B, Al-Asheh B, Hayajneh O (2000) Adsorption of phenol by bentonite. *Environ Poll* 107(3):391–398. [https://doi.org/10.1016/S0269-7491\(99\)00173-621](https://doi.org/10.1016/S0269-7491(99)00173-621)
- Brown GE, Eenrich VE, Casey WH, Clark DL, Eggleston C, Felmy A, Nealson KH (1999) Metal oxide surfaces and their interactions with aqueous solutions and microbial organisms. *Chem Rev* 99(1):77–174. <https://doi.org/10.1021/cr980011z>
- Cannata José CL, Márquez AN, Jacoby A (2011) Adsorption of phenol and nitrophenols by carbon nanospheres: Effect of pH and ionic strength Sep. *Purif Technol* 80(2):217–224
- Chen ML, Bae JS, Yoon HS, Lim CS, Oh WC (2011) The photodegradation effect of organic dye for metal oxide (Cr<sub>2</sub>O<sub>3</sub>, MgO and V<sub>2</sub>O<sub>3</sub>) treated CNT/TiO<sub>2</sub> composites. *Bull Korean Chem Soc* 32(3):815–820
- Cornell RM, Schwertmann U (2003) The iron oxides: structure, properties, reactions, occurrences and uses, 2nd edn. Wiley-VCH, Weinheim, pp 232–240
- Fan CM, Zhang LF, Wang SS, Wang DH, Lu LQ, Xu AW (2012) Novel CeO<sub>2</sub> yolk-shell structures loaded with tiny Au nanoparticles for superior catalytic reduction of p-nitrophenol. *Nanoscale* 4(21):6835–6840
- Ghose SK, Waychunas GA, Trainor TP, Eng PJ (2010) Hydrated goethite ( $\alpha$ -FeOOH) (100) interface structure: ordered water and surface functional groups. *Geochim Cosmochim Acta* 74(7):1943–1953. <https://doi.org/10.1016/j.gca.2009.12.015>
- Gimbert F, Morin-Crini N, Renault F, Badot PM, Crini G (2008) Adsorption isotherm models for dye removal by cationized starch-based material in a single component: error analysis. *J Hazard Mater* 157:34–46. <https://doi.org/10.1016/j.hazmat.2007.12.072>
- Gladysz-Plaska A (2017) Application of modified clay for removal of phenol and PO<sub>4</sub><sup>3-</sup> ions from aqueous solutions. *Adsorpt Sci Technol* 35:692–699
- Ho YS (2004) Selection of optimum sorption isotherm. *Carbon* 42:2115–2116. <https://doi.org/10.1016/j.carbon.2004.03.0159>
- Indian Standards (IS) (2012) Quality criteria for drinking water, Bureau of Indian Standards. Indian Standards, Manak Bhawan, p 10500
- Ivančev-Tumbas I, Hobby R, Küchle B, Panglisch S, Gimbel R (2008) p-Nitrophenol removal by combination of powdered activated carbon adsorption and ultrafiltration:- comparison of different operational modes. *Water Res* 42(15):4117–4124
- Jaeger S, dos Santos A, Fernandes AN, Almeida CAP (2015) Removal of p-nitrophenol from aqueous solution using Brazilian peat: kinetic and thermodynamic studies. *Water Air Soil Pollut* 226:236. <https://doi.org/10.1007/s11270-015-2500-9>
- Jin R, Xing Y, Yu X et al (2012) Facile synthesis of well-dispersed silver nanoparticles on hierarchical flower-like Ni<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> with a high catalytic activity towards 4-nitrophenol reduction. *Chemistry* 7(12):2955–2961
- Juny MW, Ahn KH, Lee Y (2001) Adsorption characteristics of phenol and chlorophenols on granular activated carbons (GAC). *Microchem J* 70:123–131
- Kung KS, McBride MB (1991) Bonding of chlorophenol on iron and aluminum oxides. *Environ Sci Technol* 25:702–709. <https://doi.org/10.1021/es00016a015>
- Lin KYA, Hsieh YT (2015) Copper-based metal organic framework (MOF), HKUST-1, as an efficient adsorbent to remove p-nitrophenol from water. *J Taiwan Inst Chem Eng* 50:223–228. <https://doi.org/10.1016/j.jtice.2014.12.008>
- Liu H, Chen T, Frost RL (2014) An overview of the role of goethite surfaces in the environment. *Chemosphere* 103:1–11. <https://doi.org/10.1016/j.chemosphere.2013.11.065>
- Magdy YM, Altaher H, ElQada E (2018) Removal of three nitrophenols from aqueous solutions by adsorption onto char ash: equilibrium and kinetic modeling. *Appl Water Sci* 8:26. <https://doi.org/10.1007/s13201-018-0666-1>
- Marais E, Nyokong T (2008) Adsorption of 4-nitrophenol onto Amberlite® IRA-900 modified with metallophthalocyanines. *J Hazard Mat* 152(1):293–301. <https://doi.org/10.1016/j.jhazmat.2007.06.096>
- McBride MB, Kung KS (1991) Adsorption of phenol and substituted phenols on iron oxide. *Environ Toxicol Chem* 40:441–448. <https://doi.org/10.1002/etc.5620100403>
- Mehrizad A, Zare K, Aghaie H, Dastmalchi DS (2012) Removal of 4-chloro-2-nitrophenol occurring in drug and pesticide waste by adsorption onto nano-titanium dioxide. *Int J Environ Sci Technol* 9(2):355–360
- Ofomaja AE, Unuabonah EI (2013) Kinetics and time-dependent Langmuir modeling of 4-nitrophenol adsorption onto Mansonia sawdust. *J Taiwan Inst Chem Eng* 44:566–576. <https://doi.org/10.1016/j.jtice.2012.12.021>
- Ouardi ME, Laabd M, Oualid HA, Brahmi Y, Abamrane A, Elouahli AAA, Laknifi A (2019) Efficient removal of p-nitrophenol from water using montmorillonite clay: insights into the adsorption mechanism, process optimization, and regeneration. *Environ Sci Pollut Res* 26:19615–19631. <https://doi.org/10.1007/s11356-019-05219-6>
- Pham TH, Lee BK, Kim J (2016) Improved adsorption properties of a nano zeolite adsorbent toward toxic nitrophenols. *Process Saf Environ Prot* 104:314–322. <https://doi.org/10.1016/j.psep.2016.08.018>
- Polat H, Molva M, Polat M (2006) Capacity and mechanism of phenol adsorption on lignite. *Int J Miner Process* 79(4):264–273. <https://doi.org/10.1016/j.minpro.2006.03.003>

- Qiu X, Zhong Q, Li M, Bai W, Li B (2007) Biodegradation of *p*-nitrophenol by methyl parathion-degrading *Ochrobactrum* sp. B2. *Int Biodeter Biodegrad* 59(4):297–301. <https://doi.org/10.1016/j.ibiod.2006.09.005>
- Qiu LH, Peng YJ, Liu BQ, Lin BC, Malik MJ, Yan F (2012) Polypyrrole nanotube-supported gold nanoparticles: an efficient electrocatalyst for oxygen reduction and catalytic reduction of 4-nitrophenol. *Appl Catal A* 413–414:230–237
- Ramírez EEP, Asunción VS, Mde-La R, Hernández ALM, Santos CV (2017) Removal of phenolic compounds from water by adsorption and photocatalysis. *InTech*, London, p 347. <https://doi.org/10.5772/66895>
- Senturk HB, Ozdes D, Gundogdu A, Duran C, Soylak MJ (2009) Removal of phenol from aqueous solutions by adsorption onto organomodified tirebolu bentonite : equilibrium, kinetic and thermodynamic study. *Hazard Mat* 172(1):353–362. <https://doi.org/10.1016/j.jhazmat.2009.07.019>
- Simonin JP (2016) On comparison of pseudo-first order and pseudo-second order rate laws in the modeling of adsorption kinetics. *Chem Eng J* 300:254–263. <https://doi.org/10.1016/j.cej.2016.04.079>
- Sparks DL (1998) *Soil physical chemistry*, 2nd edn. CRC Press, Boston, p 100. <https://doi.org/10.1016/j.seppur.2011.04.029>
- Tejedor-Tejedor MI, Yost EC, Anderson MA (1992) Characterization of benzoic and phenolic complexes at the goethite/aqueous solution interface using cylindrical internal reflection. *Langmuir* 8(2):525–533. <https://doi.org/10.1021/la00038a036>
- Tran HH, Roddick FA, O'Donnell JA (1999) Comparison of chromatography and desiccant silica gels for the adsorption of metal ions-I. Adsorption and kinetics. *Water Res* 33(13):2992–3000. [https://doi.org/10.1016/S0043-1354\(99\)00017-2](https://doi.org/10.1016/S0043-1354(99)00017-2)
- USEPA (1980) Environmental Protection Agency (EPA) ambient water quality criteria for nitrophenols. USEPA, Washington
- Varank G, Demir A, Yetilmezsoy K, Top S, Sekman E, Bilgili MS (2012) Removal of 4-nitrophenol from aqueous solution by natural low-cost adsorbents. *Ind J Chem Technol* 19:7–25
- Wang S, Qiao N, Yu J, Huang X, Hu M, Ma H (2014) Effect of ionic strength on the adsorption behavior of phenol over modified activated clay. *Desalin Water Treat* 57(9):4174–4182. <https://doi.org/10.1080/19443994.2014.989269>
- Xiong P, Fu Y, Wang L, Wang X (2012) Multi-walled carbon nanotubes supported nickel ferrite: a magnetically recyclable photocatalyst with high photocatalytic activity on degradation of phenols. *Chem Eng J* 195–196:149–157
- Yuan-Xiang Y, He-Bing L, Jin-Yun L, Xin-Liang T, Jin-Gang Y, Zhi-Guang P (2014) Removal and adsorption of *p*-Nitrophenol from aqueous solutions using carbon nanotubes and their composites. *J Nanomater* 2014:1–9. <https://doi.org/10.1155/2014/571745>

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.