



Removal of Pb(II) and Cr(VI) by laterite soil from synthetic waste water: single and bi-component adsorption approach

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ABSTRACT

Adsorption of Pb(II) and Cr(VI) on laterite soil adsorbent from aqueous solution has been studied as a function of pH, contact time, adsorbent dose, and initial concentration through single and bi-component approach in batch reactor. The optimum conditions for both metals are found as pH 6, contact time 240 min, adsorbent dose 10 g/L, and initial concentration 20 mg/L for single component adsorption. Kinetics and equilibrium adsorption data of single component adsorption fit well to the pseudo-second-order kinetic model and Freundlich isotherm model, respectively. Under the experimental conditions, adsorption of Pb(II) is found to be more than that of Cr(VI) for both single component and bi-component systems. The combined adsorptions of Pb(II) and Cr(VI) in single and bi-component systems do not differ much. The extended Freundlich model is found to best represent the equilibrium adsorption phenomena in bi-component system.

Keywords: Adsorption kinetic; Chromium; Lead; Bi-component isotherm; Wastewater

1. Introduction

Heavy metals are highly toxic, non-biodegradable, and conservative pollutants, which enter water stream mainly through various industrial and natural sources. Due to conservative nature of heavy metals, prolonged consumption of contaminated water containing even small amount of heavy metals may cause serious health impacts. Out of various heavy metals, Pb(II) and Cr(VI) are recognized as long lasting environmental pollutants, which are generated mainly by process industry such as battery manufacturing, metal plating, tanning, finishing, leather industries, glass industry as well as natural sources [1,2]. A long exposure to these

metals may cause many serious disorders on human health such as sickness, fatigue, anemia, kidney disease, nervous disorder. and even death. Therefore, to reduce the chance of disease on metal exposure, WHO has set maximum permissible limits of lead and total chromium in drinking water are 0.01 and 0.05 mg/L, respectively [3], while according to Indian standard, the corresponding values are 0.05 mg/L for both the metals [4].

Various physicochemical techniques are available for heavy metals removal such as coagulation [5], membrane separation [6], electro dialysis [7], ion exchange [8,9]. These techniques are expensive and include intricate operations and require high maintenance cost. The other drawbacks are sludge generation and disposal, high requirement of chemicals, and

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membrane fouling, etc. Adsorption processes have the potential to avoid these difficulties. Many adsorbents have been used for the treatment of heavy metals containing water/waste water [10,11]. In most of the papers dealing with the adsorption of Pb(II) and Cr(VI), these metals have been used separately [1,12–16]. However, both of these metals exist simultaneously in some industrial effluents such as waste water from metal finishing industries [17]. Since, both the metals are positively charged, they may experience some sort of competition for simultaneous adsorption on active sites of adsorbent. However, hardly any literature is available on the simultaneous removal of these heavy metals. Further, efforts are on to use low cost natural material as adsorbent to reduce the cost of the process. Laterite soil is naturally available and contains good amount of SiO_2 , Fe_2O_3 , Al_2O_3 , etc. which can create both positive and negative charges on the surface of laterite at neutral pH, although the relative amount of positive charges changes with pH. Thus, it can be used to remove Pb(II) and Cr(VI) under certain pH. Nevertheless, there is hardly any literature on the simultaneous removal of these metals using laterite soil.

The aims of present study are to (i) study the performance of laterite soil for the removal of Pb(II) and Cr(VI), (ii) characterization of the adsorbent, (iii) study the effect of process parameters such as pH, time, initial concentration of Pb(II) and Cr(VI), adsorbent dose on the removal of Pb(II) and Cr(VI), (iv) find out the kinetic constants, (v) determine the applicability of isotherm model, (vi) determine the applicability of bi-component adsorption isotherm in bi-component system.

2. Materials and methods

2.1. Reagents

Stock solutions of Pb(II) and Cr(VI) were prepared from lead nitrate and potassium dichromate, respectively. All reagents used in the present experiments were of analytical grade (AR). Distilled water was used for dilution.

2.2. Preparation of adsorbent

Laterite soil, procured from Burdwan district of West Bengal, was dried for a period of 2 d to remove the moisture. It was then rinsed well with distilled water until the dirt particles were removed and the wash water became colorless. It was then dried in the oven at 110°C and put through various mesh sizes for sieving purposes. Based on the literature review,

particle sizes were taken in the range of 0.6–0.85 mm. Screened material was then stored in a covered beaker and further used in experiments as an adsorbent [18].

2.3. Characterization of adsorbent

Fourier transform infrared spectrometer (FTIR, Nicolet 6700, USA) was used to find out the type of functional groups present in the adsorbent. Scanning electron microscopy (SEM) (LEO 435 VP) study was conducted to observe the morphology of adsorbent surface before and after the metal uptake. The surface area, pore size, and pore volume of the adsorbent were measured by Brunauer–Emmett–Teller isotherm (BET) (ASAP 2020 V3.05 H Micromeritics system) and XRD pattern was developed by using X-ray diffractometer (BRUKER D8 ADVANCE). XRD data were analyzed using PANalytical X'Pert HighScore software version 1.0e.

2.4. Analytical methods

The concentrations of Pb(II) and Cr(VI) were determined by atomic absorption spectrometry AAS (GBC Avanta M, Flame: air-acetylene).

2.5. Batch adsorption studies

The stock solutions of Pb(II) and Cr(VI) were used to prepare solutions containing Pb(II) and Cr(VI) separately as 5, 10, 15, and 20 mg/L, respectively. The experiments were carried out separately in batch mode in 100-ml conical flasks at a temperature of 305 K and 150 rpm. Orbital shaker was used for agitation purpose. The adsorbent particle size was taken in the range of 0.6–0.85 mm for laterite soil. The effects of initial concentration, pH, contact time, and adsorbent dose were studied as shown in Table 1. After filtration, the clear solution was used to determine the Pb(II) and Cr(VI) concentration using atomic absorption spectrometer. All the adsorption experiments were performed in triplicate and the average values are recorded.

Data obtained under varying time were used to compute kinetic parameters. Data obtained under varying initial metal concentration were used to compute isotherm constants.

Bi-component mixture containing Pb(II) and Cr(VI) were prepared by mixing individual solution of Pb(II) and Cr(VI) of desired concentration in desired ratio and experiments were conducted in similar way as described above. Extended Freundlich models as expressed through Eqs. (1) and (2) were tested for

Table 1

Range of operating parameters for Pb(II) and Cr(VI) adsorption by laterite soil

Type of experiment	pH	Adsorbent dose (g/L)	Contact time (min)	Initial Pb(II) concentration (mg/L)	Initial Cr(VI) concentration (mg/L)
Effect of pH	2–10	10	240	20	20
Effect of adsorbent dose	6	5–40	240	20	20
Effect of contact time	6	10	0–300	20	20
Effect of initial ion concentration	6	10	240	5–20	5–20

explaining equilibrium adsorption of bi-component system:

$$q_{e,1} = \frac{K_{F,1} C_{e,1}^{\left(\frac{1}{n_1}\right) + x_1}}{C_{e,1}^{x_1} + y_1 C_{e,2}^{z_1}} \quad (1)$$

$$q_{e,2} = \frac{K_{F,2} C_{e,2}^{\left(\frac{1}{n_2}\right) + x_2}}{C_{e,2}^{x_2} + y_2 C_{e,1}^{z_2}} \quad (2)$$

where $K_{F,1}$, $K_{F,2}$, n_1 and n_2 were obtained from corresponding individual Freundlich isotherm equation while x_1 , x_2 , y_1 , y_2 , z_1 , and z_2 are bi-component Freundlich adsorption isotherm constants of Pb(II) and Cr(VI), respectively.

The equilibrium solid phase concentration of each adsorbate in a bi-component system, percentage removal of individual adsorbate, percentage removal of total adsorbate, and percentage error were calculated from the Eqs. (3)–(6), respectively.

$$q_{e,i} = \frac{(C_{o,i} - C_{e,i})V}{m} \quad (3)$$

$$Ad_i \% = \frac{(C_{o,i} - C_{e,i})}{C_{o,i}} \times 100 \quad (4)$$

$$Ad_{total} \% = \frac{\sum (C_{o,i} - C_{e,i})}{\sum C_{o,i}} \times 100 \quad (5)$$

$$Error \% = \frac{(\text{Experiment value} - \text{Predicted value}) \times 100}{\text{Experimental value}} \quad (6)$$

where $q_{e,i}$ is solid phase equilibrium concentration of each adsorbate in a dual component mixture (mg/g), $C_{o,i}$ is initial concentration of each component (mg/L), $C_{e,i}$ is equilibrium concentration of each component (mg/L), V is volume of the adsorbate containing solution (L), and m is mass of the adsorbent (g). The

isotherm model data of bi-component adsorption of Pb(II) and Cr(VI) were determined using the STATISTICA 8 software.

3. Results and discussion

3.1. Characteristics of adsorbent

3.1.1. XRD Pattern of adsorbent

The XRD pattern of laterite soil is presented in Fig. 1. The peak at $2\theta = 32$, 67 are due to the presence of Fe_2O_3 . Whereas the presence of $FeO(OH)$ and FeO can be anticipated by the peaks at $2\theta = 21$, 26, 36, 63, and $2\theta = 36$, 42, 61, respectively. Peaks at $2\theta = 37$, 45, 66 indicate $Al_{2.66}O_4$ and at $2\theta = 45$, 66 represent Al_2O_3 . Other peaks at $2\theta = 20$, 26, 39, 50, 59, and 68 correspond to SiO_2 . The peaks at $2\theta = 18$, 21, 62 are probably due to Fe_3O_4 .

3.1.2. Surface characteristics

The surface characteristics of laterite soil adsorbent determined by BET surface analyzer are shown in Table 2.

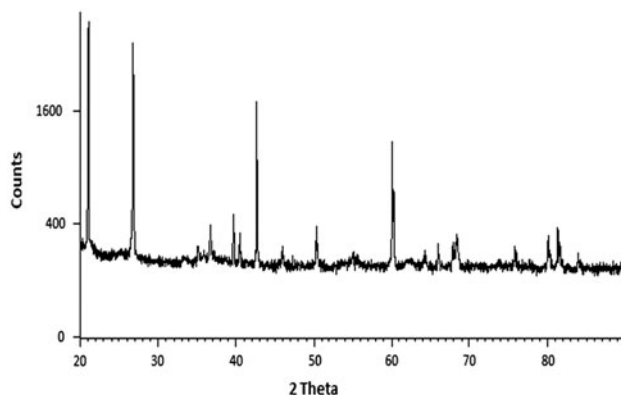


Fig. 1. X-ray diffraction pattern of laterite soil adsorbent.

3.1.3. FTIR analysis

The FTIR spectra of laterite soil are shown in Fig. 2. The presence of iron, aluminum, and silicon oxides or hydroxides gets confirmed by studying spectral peaks. The bands at 3,624.22 and 3,428.9 cm^{-1} signify the presence of OH group of Si, Al. The band at 1,627.16 cm^{-1} represents the presence of inner layer water molecules. The bands at 1,034.49, 913.38, and 788.32 cm^{-1} are due to the presence of Si–O–Fe, Al–OH, Fe–OH vibrations. The bands at 534.21, 467.25, and 441.61 cm^{-1} signify the presence of Hematite (Fe–O bond stretching). These bands have also been reported with slight variation for laterite soil by Maiti et al. [19].

3.1.4. Scanning electron microscopy

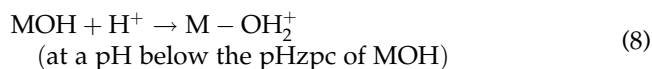
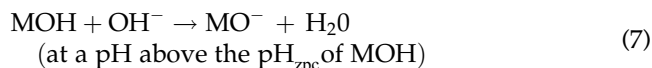
The SEM is used to study the changes in morphology of the adsorbent surface due to addition of metals; SEM of the adsorbent before and after the adsorption is shown in Fig. 3. SEM before adsorption as shown in Fig. 3(a) indicates the heterogeneous structure of laterite soil. The change in surface morphology of laterite soil after Pb(II) and Cr(VI) adsorption is evident by comparing the SEM as shown in Fig. 3(a) and (b).

3.2. Effect of pH

Effect of pH on the removal of both Pb(II) and Cr(VI) as shown in Fig. 4 indicates that for both the metal ions, % removal is maximum at pH around 6 and least at pH around 10 within the investigated pH range. Optimum removal of Pb(II) and Cr(VI) at pH 6 is found to be 95 and 74%, respectively. Metal ion adsorption on laterite soil depends on pH of solution; it can be increased or reduced by the initial pH of the solution due to interaction of metal ions with adsorbed surface functional group on the soil surface. Variation in ionic character of adsorbent also plays important role on adsorption.

Laterite soil contains SiO_2 ($\approx 40\%$), Fe_2O_3 ($\approx 45\%$), Al_2O_3 ($\approx 15\%$), Mn_2O_3 ($\approx 2\%$), etc. [20]. The pHzpc of these oxides are 2.2, 8.0, 8.3, and 4.0, respectively

[21,22]. The above oxides undergo following reactions depending upon the pH of the solution and create +ve as well as –ve charges.



Here, MOH represents the metal hydroxides.

In the present case, in 50 ml solution, 0.5 g laterite soil is used. Thus, moles of SiO_2 , Fe_2O_3 , Al_2O_3 , and Mn_2O_3 , etc. present in the laterite soil are 3.33×10^{-3} , 1.41×10^{-3} , 7.35×10^{-4} , and 6.33×10^{-5} , respectively. On the basis of the above data, Fig. 5 can be developed to explain the changes in the surface charge characteristics of adsorbent with variation in solution pH. It seems that at lower pH (< 2.2), the surface of the adsorbent is strongly positively charged, which decreases with increase in solution pH. As shown in Fig. 5, it is evident that above pH 8.3, the surface is strongly negatively charged.

Considering the solution-phase chemistry of Pb(II) [23], it is evident that it exists predominantly as Pb^{2+} at lower pH, which is gradually converted to PbOH^+ with increase in solution pH. Above pH 6, Pb(II) predominantly exists as PbOH^+ and is converted to PbO (aq) with increase in pH up to pH 11. Further, large number of negative sites is available on adsorbent surface at pH 6 as evident from Fig. 5. It may be possible that the present experiment provides sufficient energy to the Pb(II) moiety for its transport to the bulk of the solution to the surface of the adsorbent. Above pH 6, although the negative sites on adsorbent surface increases, the positive charge on Pb(II) species also decreases, as a result, maximum removal is achieved at the pH value of around 6. Increase in Pb(II) removal from pH 2–6 is due to the increase in negative charge on adsorbent surface due to creation of negative sites by SiO_2 and Mn_2O_3 as per Eq. (7) above pH 2.2 and 4, respectively.

It is reported that Cr(VI) can be converted to Cr(III) under acidic condition [12]. Thus, in the present case, some Cr(VI) may be partially converted to Cr(III). As per the Eh-pH diagram reported by Lindsay et al. [24], Cr(VI) exists predominantly as HCrO_4^- within pH 2–6.5, and above pH 6.5, it exists predominantly as CrO_4^{2-} . Whereas Cr(III) exists predominantly as Cr^{3+} within the pH range of 2–4 and predominantly as Cr^{2+} within pH 2–8. Overall removal of Chromium is maximum at the pH value around 6 where Cr(VI) exists as most negatively charged and Cr(III) exists as

Table 2
Characteristics of laterite soil

Properties	Raw laterite
Particle size (mm)	0.6–0.85
Surface area (m^2/g)	23.015
Monolayer volume (cm^3/g)	5.287
Total pore volume (m^3/g)	0.011

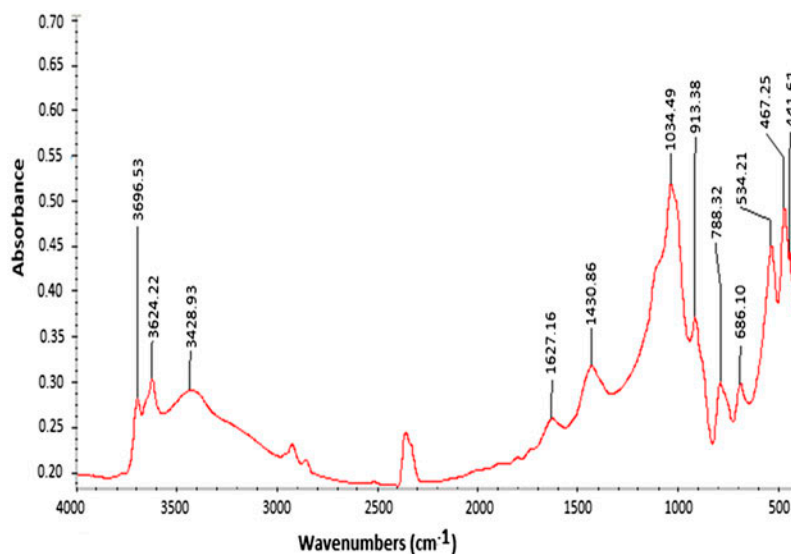


Fig. 2. FTIR spectrum of laterite soil adsorbent.

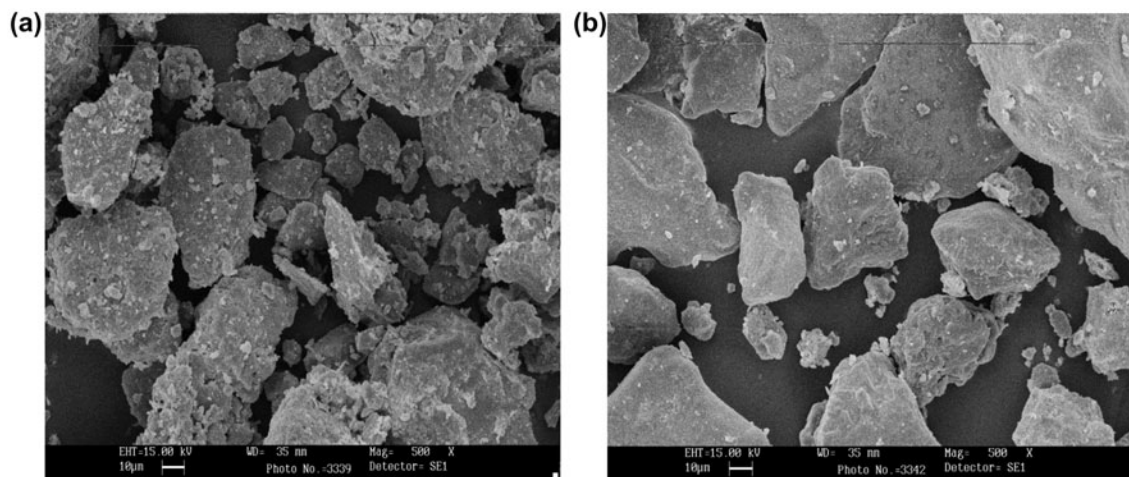


Fig. 3. SEM characterizations of laterite soil adsorbent, (a) before and (b) after adsorption.

less positively charged, when surface of adsorbent contains large number of positive sites. The agitation of the present experiment may be able to provide sufficient energy to overcome the repulsion between positively charged Cr(III) species and the positive sites of the adsorbents at pH 6. Above pH 8.3, the surface of adsorbent becomes more negative as shown in Fig. 5; consequently, the percentage removal of Cr(VI) and Cr(III) above this pH is very less.

3.3. Effect of adsorbent dose

To know the effect of adsorbent dose on percentage removal of both metals, experiments have been

performed as per the conditions mentioned in Table 1. From Fig. 6, it is elucidated that percentage removals of Pb(II) and Cr(VI) increase with increase in adsorbent dose from 5 to 10 g/L and considerably remain constant above the 10 g/L of adsorbent dose. With increase in adsorbent dose, more active sites are added in the solution, and thus, adsorption increases initially. However, after 10 g/L since the majority of the metal ions are adsorbed, the driving force (concentration gradient) to bring the metal ions from the bulk of the solution to the adsorbent surface decreases. Due to this reason, increase in adsorbent dose does not increase the percentage removal much above 10 g/L of adsorbent dose.

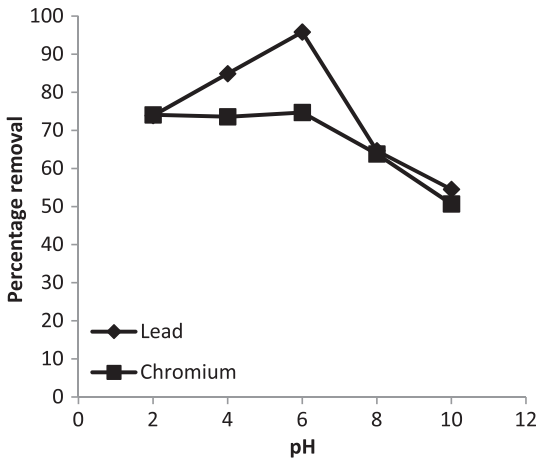


Fig. 4. Effect of pH on percentage removal of Pb(II) and Cr(VI) (adsorbent dose: 10 g/L, initial concentration: 20 mg/L, contact time: 240 min, shaker speed: 150 rpm).

3.4. Effect of contact time

Fig. 7 shows the effect of contact time on adsorption of Pb(II) and Cr(VI) by laterite soil. From Fig. 7, it is evident that initially the percent removal of both metals increases rapidly with the time up to 120 min and after that it increases gradually and finally reaches equilibrium value. For both the cases, equilibrium between the adsorbent and adsorbate in solution is achieved at 240 min. The maximum removals of Pb

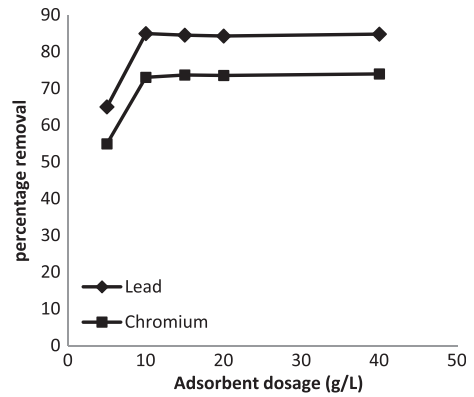


Fig. 6. Effect of adsorbent dose on percentage removal of Pb(II) and Cr(VI) (pH 6, initial concentration: 20 mg/L, contact time: 240 min, shaker speed: 150 rpm).

(II) and Cr(VI) by laterite soil at equilibrium are 1.92 and 1.51 mg/g, respectively.

3.5. Effect of initial concentration

Initial concentration is an important parameter which affects the adsorption of heavy metals on laterite soil. To understand the effect of initial concentration of heavy metals, experiments have been performed as per conditions mentioned in Table 1. It is clearly observed from Fig. 8 that q_e increases with increase in initial concentration for both the metals.

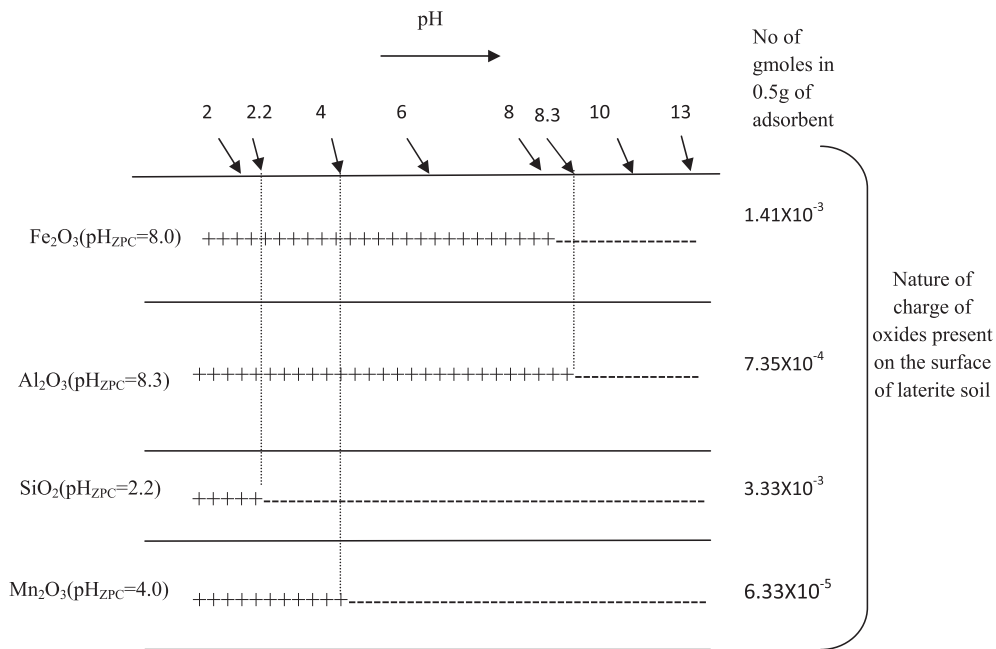


Fig. 5. Contribution of various oxides of laterite soil on the overall surface charge at various pH.

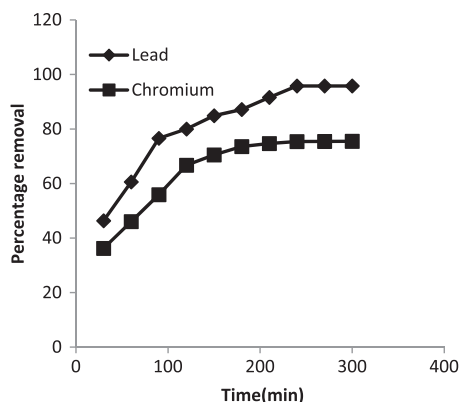


Fig. 7. Effect of contact time on percentage removal of Pb(II) and Cr(VI) (pH 6, initial concentration: 20 mg/L, adsorbent dose: 10 g/L, shaker speed: 150 rpm).

Linear nature of the line in Fig. 8 indicates the active sites are not saturated even with 20 mg/L metal concentration. However, for further studies, 20 mg/L of initial concentration of both metals were selected as in industrial waste water the concentration of Pb(II) and Cr(VI) are normally found as ≤ 20 mg/L [13,25].

3.6. Adsorption kinetics

Table 3 represents the kinetic parameters of various models for Pb(II) and Cr(VI) adsorption on laterite soil. From Table 3, it is evident that the pseudo-second-order model gives better fit to the experimental data for both Pb(II) and Cr(VI) adsorption with R^2 values of 0.995 and 0.976, respectively. Therefore, it may be concluded that Pb(II) and Cr(VI) adsorption on laterite soil follows a chemisorption/ion exchange mechanism.

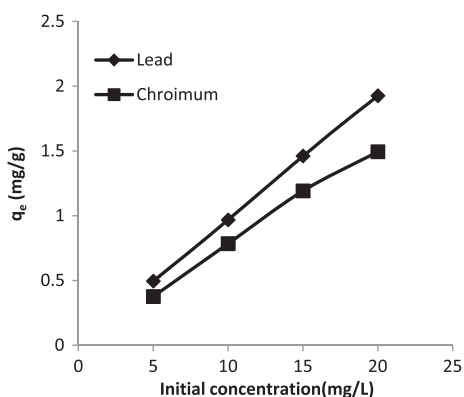


Fig. 8. Effect of initial concentrations on q_e of Pb(II) and Cr(VI) (pH 6, adsorbent dose: 10 g/L, contact time: 240 min, shaker speed: 150 rpm).

To understand the intra particle diffusion of Pb(II) and Cr(VI) on adsorbent q_t vs $t^{1/2}$ plots has been developed as shown in Fig. 9. From Fig. 9, it is evident that the plots for both metals show the similar multilinearity (having two linear parts P1, and P2), which indicates that pore diffusion does not solely control the Pb(II) and Cr(VI) adsorption process.

Elovich model describes the chemisorption phenomena of adsorption process [22]. q_t vs. $\ln(t)$ plot has been developed as shown in Fig. 10. The correlation coefficients of Pb(II) and Cr(VI) are found as 0.970 and 0.941, respectively, which show the fitness of Elovich model. Furthermore, pseudo-second-order kinetic model also supports the possibility of chemisorption in the present case [14].

3.7. Single component adsorption isotherm

In this study, both the Langmuir and the Freundlich isotherms are examined, but the Freundlich isotherm gives a better goodness of fit (R^2 value for Pb(II): 0.988, Cr(VI): 0.970). The various parameters of Langmuir and Freundlich model for Pb(II) and Cr(VI) adsorption are given in Table 4.

3.8. Single and bi-component adsorption of Pb(II) and Cr(VI)

To determine the effect of initial concentration of Pb(II) and Cr(VI) on the equilibrium uptake of Pb(II), the initial Pb(II) concentrations were varied between 5 and 20 mg/L, while the initial Cr(VI) concentration in each adsorption process was held constant at 0, 5, 10, 15, 20 mg/L. The experimental results as shown in Table 5 clearly indicate that the uptake of Pb(II) ions increases with the increase in initial concentration of Pb(II). The equilibrium uptake of Pb(II) ion reduces slightly with the increasing concentration of Cr(VI) ions. At 20 mg/L initial Pb(II) concentration, in the absence of Cr(VI) ions and in the presence of 20 mg/L Cr(VI) ions, adsorbed equilibrium Pb(II) quantities were found as 1.92 and 1.84 mg/g, respectively.

Further, the initial concentration of Cr(VI) ions has varied from 5 to 20 mg/L while initial Pb(II) concentration was held constant between 0 and 20 mg/L for each experiment and results are shown in Table 5. Equilibrium uptake of Cr(VI) increases with the increase in initial concentration of Cr(VI) up to 20 mg/L, but increase of Pb(II) concentration slightly reduces the Cr(VI) adsorption. At 20 mg/L of initial Cr(VI) concentration, in the absence of Pb(II) ions and in the presence of 20 mg/L Pb(II) ions, adsorbed Cr(VI) quantities at equilibrium were found 1.51 and 1.47 mg/g, respectively.

Table 3

Parameters of various kinetic models for adsorption of Pb(II) and Cr(VI) on laterite soil

Model	R^2	Kinetic parameter
<i>For Pb(II)</i>		
Pseudo-first-order	0.726	K_1 (min^{-1}): 0.036
Pseudo-second-order	0.995	K_2 ($\text{g}/(\text{mg min})$): 8.91×10^{-3}
Weber and Morris model	0.930	K_{id} ($\text{mg}/\text{g min}^{-1/2}$): 0.085
Elovich model	0.970	I (mg/g): 0.5658 α ($\text{mg}/(\text{g min})$): 0.113 β (g/mg): 2.169
<i>For Cr(VI)</i>		
Pseudo-first-order	0.964	K_1 (min^{-1}): 0.022
Pseudo-second-order	0.976	K_2 ($\text{g}/(\text{mg min})$): 8.43×10^{-3}
Weber and Morris model	0.880	K_{id} ($\text{mg}/\text{g min}^{-1/2}$): 0.070
Elovich model	0.941	I (mg/g): 0.432 α ($\text{mg}/(\text{g min})$): 0.059 β (g/mg): 2.958

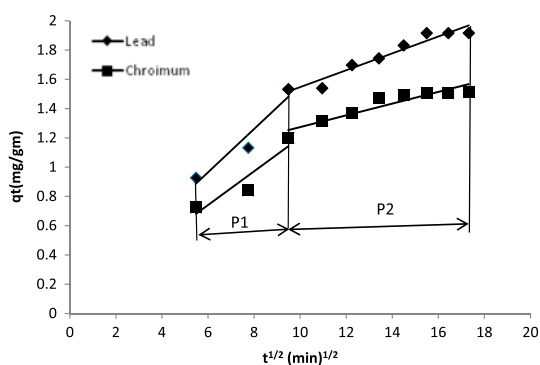


Fig. 9. Weber and Morris model [26] for adsorption of Pb(II) and Cr(VI) using laterite soil

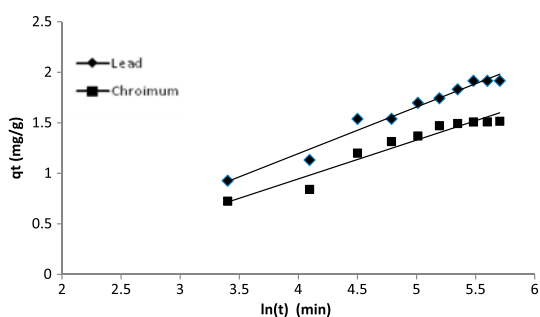


Fig. 10. Plot of Elovich model for adsorption of Pb(II) and Cr(VI) using laterite soil.

Bi-component adsorption possesses generally shows three possible types of behavior: synergism-in mixture; the mixture, effect is greater than the single

component; antagonism-in mixture, effect is less than that of single components; non-interaction-in mixture, have no effect on single component in a mixture. To analyze the sorption behavior of Pb(II) and Cr(VI) components, the adsorption yield of single and bi-component are also compared. From Table 5, it is expected that the total adsorption yield must be equal to 85.88% for the total metal concentration of 40 mg/L containing 20 mg/L of equal concentrations of Pb(II) and Cr(VI) in the mixture [AdTot % = 85.88 = 100 × [(19.19 mg/L Pb(II) + 15.15 mg/L Cr(VI) ion)/40 mg/L initial total concentration] if there is no interaction. However, the experimental total adsorption yield obtained is found to be 83.01% [AdTot % = 83.01 = 100 × [(18.46 mg/L Pb(II) + 14.73 mg/L Cr(VI))/40 mg/L initial total concentration] in bi-component system. Thus, it becomes clear that for the bi-component system, interaction between Pb(II) and Cr(VI) ions is not significant as the difference between experimental and expected total adsorption is less (~2%).

The experimental data obtained from single and bi-component adsorption of Pb(II) and Cr(VI) as shown in Table 5. Indicate that the Pb(II) removal is higher as compared to Cr(VI) removal on laterite soil. Fitting of second-order kinetics indicates the possibilities of chemisorption/hydroxyl ion exchange. Thus, it seems that ion exchange mechanism may play significant role on Pb(II) adsorption on laterite soil. In general, the adsorption of particular species depends on many factors such as type of functional group, point of zero charge, surface properties of sorbent, properties of sorbate like concentration, molecular structure,

Table 4

Langmuir and Freundlich isotherm parameter for adsorption of Pb(II) and Cr(VI) on laterite soil

Langmuir isotherm parameters						
Constants for Pb(II)				Constants for Cr(VI)		
Temp (K)	K_L (L/mg)	q_{max} (mg/g)	R^2	K_L (L/mg)	q_{max} (mg/g)	R^2
300	2.20	2.95	0.904	0.017	19.49	0.067

Freundlich Adsorption isotherm parameters						
Temp (K)	K_f (mg/g)(mg/L) ⁿ	n	R^2	K_f (mg/g) (mg/L) ⁿ	n	R^2
300	2.47	1.620	0.988	0.327	0.997	0.970

Table 5

Comparison of the individual and total adsorption equilibrium specific uptake of metals and their yields found at different Pb(II) concentration in the presence and absence of increasing Cr(VI) concentration on laterite soil at 300 K

$C_{o,Pb}$ (mg/L)	$C_{o,Cr}$ (mg/L)	$C_{e,Pb}$ (mg/L)	$C_{e,Cr}$ (mg/L)	$q_{e,Pb}$ (mg/g)	$q_{e,Cr}$ (mg/g)	Ad _{Pb} %	Ad _{Cr} %	Ad _{Total} %
5	0	0.076	0	0.492	0	98.48	0	98.48
10	0	0.289	0	0.962	0	97.11	0	97.11
15	0	0.392	0	1.459	0	97.38	0	97.38
20	0	0.804	0	1.920	0	95.98	0	95.98
0	5	0	1.242	0	0.375	0	75.16	75.16
5	5	0.045	1.159	0.495	0.384	99.1	76.82	87.96
10	5	0.323	1.209	0.967	0.379	96.77	75.82	89.78
15	5	0.387	1.232	1.461	0.376	97.42	75.36	91.91
20	5	0.738	1.242	1.920	0.375	96.31	75.16	92.08
0	10	0	2.086	0	0.791	0	79.14	79.14
5	10	0.289	2.806	0.471	0.719	94.22	71.94	79.36
10	10	0.582	2.117	0.941	0.788	94.18	78.83	86.51
15	10	0.614	2.156	1.438	0.784	95.91	78.44	88.92
20	10	0.894	2.332	1.910	0.766	95.53	76.68	89.25
0	15	0	3.722	0	1.127	0	75.18	75.18
5	15	0.651	3.055	0.434	1.194	86.98	79.63	81.47
10	15	0.874	3.655	0.912	1.134	91.26	75.63	81.88
15	15	0.921	3.722	1.407	1.127	93.86	75.19	84.52
20	15	1.122	3.803	1.887	1.119	94.39	74.64	85.93
0	20	0	4.844	0	1.511	0	75.78	75.78
5	20	0.804	4.844	0.419	1.515	83.92	75.78	77.41
10	20	1.012	4.919	0.898	1.508	89.88	75.41	80.23
15	20	1.206	5.063	1.379	1.493	91.96	74.69	82.09
20	20	1.532	5.263	1.846	1.473	92.34	73.69	83.01

Table 6

Extended Freundlich bi-component isotherm parameter values at different temperature for simultaneous adsorption of Pb(II) and Cr(VI) removal on laterite soil

For Pb(II)				For Cr(VI)			
Temp (K)	300	305	315	Temp (K)	300	305	315
x_1	3.302	5.136	5.331	x_2	1.578	0.278	1.825
y_1	0.004	0.0004	0.0003	y_2	0.006	0.106	0.418
z_1	3.910	5.345	5.608	z_2	1.876	0.671	4.693

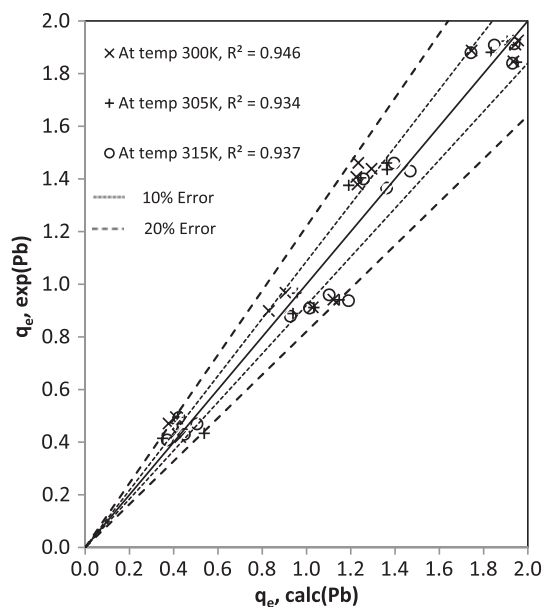


Fig. 11. Comparison of the calculated and experimental q_e values of Pb(II) ions in a bi-component mixture of Pb(II) and Cr(VI) ions.

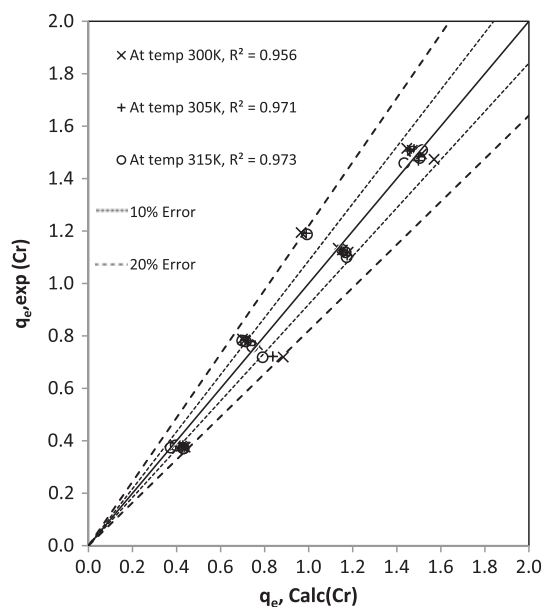


Fig. 12. Comparison of the calculated and experimental q_e values of Cr(VI) ions in a bi-component mixture of Pb(II) and Cr(VI) ions.

ionic size, interaction of different species in solution, pH [15]. Considering the above facts, it is very difficult to identify a specific factor which is responsible

for high Pb(II) removal but it may be due to the presence of high silicate in laterite soil [16].

3.9. Bi-component adsorption isotherm

The simultaneous adsorption data as shown in Table 5 of Pb(II) and Cr(VI) well fitted to extended Freundlich bi-component isotherm model. The parametric values of model are given in Table 6. The comparison of calculated and experimental values of q_e for Pb(II) and Cr(VI) are also presented in parity plots Figs. 11 and 12. It can be seen from Figs. 11 and 12 that most of the data points are distributed around the 45° line, which indicates that extended Freundlich adsorption model better represents the experimental data for bi-component adsorption. The R^2 values for Pb(II) and Cr(VI) at three different temperatures are found in the range of 0.934–0.946 and 0.956–0.973, respectively. Single component adsorption data can be well presented by Freundlich adsorption equation. Modification of the Freundlich equation as given by extended Freundlich model takes into account the interactive effects of individual Pb(II) and Cr(VI) metal ions between themselves. Therefore, the bi-component adsorption of metal ions onto laterite soil is represented satisfactorily and adequately by the extended Freundlich model.

4. Conclusions

Laterite soil, abundantly available in nature, is used in present work for the removal of Pb(II) and Cr(VI) metal ions from aqueous solution, and removal efficiency of these metals are found as 95 and 74%, respectively, for single component adsorption under optimum conditions. The experimental single component adsorption data are well represented by Freundlich isotherm and process follows the second-order kinetics. Bi-component adsorption studies reveal that the interaction effect is not significant in mixture. Extended Freundlich model best represents the bi-component experimental adsorption data.

Abbreviations

AAS	— atomic absorption spectrometry
BET	— Brunauer–Emmett–Teller
FTIR	— Fourier transform infrared spectrometer
SEM	— scanning electron microscopy
WHO	— World Health Organisation
XRD	— X-ray diffractometer

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