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Adsorptive removal of phosphorus(V) and chromium(VI) oxyanions using thermally treated titanium-rich bauxite

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ABSTRACT

The removal of P(V) and Cr(VI) oxyanions from their aqueous solution by batch adsorption technique using raw and heat-treated titanium-rich bauxite (TRB) of Jobhipat bauxite mines, Jharkhand, India, was investigated under varying experimental parameters. TRB, calcined at 450˚C (TRB-450), showed maximum uptake of both the oxyanions from their aqueous solutions. Adsorption process was found to be highly pH dependent. The optimum pH range for maximum P(V) adsorption was 4.5–5.0 while highest adsorption of Cr(VI) was observed at lower pH (~3.0) which progressively decreased on further increase of pH. Kinetic studies in the temperature range 30–50˚C revealed the adsorption of both the oxyanions were best fitted with pseudo-second-order kinetic model and Langmuir adsorption isotherms. The derived Gibbs's free energy (ΔG°) values indicated a spontaneous adsorption process for both the oxyanions, and the adsorption of P(V) ion was favoured at higher temperature while ~40˚C was found to be the optimum temperature for adsorption of Cr(VI) oxyanion. The adsorption of both oxyanions was significantly affected in the presence of bivalent anion like ions SO_4^{2-} and CO_3^{2-}. The present set of data provided further input to assess the potential of naturally occurring TRB towards the removal of different toxic ions from contaminated water.

Keywords: Adsorption; Oxyanions; Bauxite; P(V); Cr(VI)

1. Introduction

Elevated levels of several oxyanions in water bodies have become a serious concern worldwide as many of them are harmful to both humans and wildlife. Phosphate and chromate are two of such commonly occurring oxyanions that have structural resemblance and similar proton affinities but with altogether different biochemical behaviour. Phosphate is an essential, often limiting, macronutrient for growth of organisms in most ecosystems while its presence in excess causes the algal bloom in the receiving water bodies that leads to the depletion of dissolved oxygen content (eutrophication). The maximum phosphate discharge limits (<2.0 mgP L^{-1}) in treated wastewaters from municipalities and industrial effluents is still enough for eutrophication [1]. The removal of phosphate from

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the aquatic system is, therefore, important to control eutrophication. On the other hand, hexavalent chromium is toxic to all forms of life including humans and exhibits mutagenic, teratogenic and carcinogenic effects on biological systems due to its strong oxidising nature and mobility both in soil and aquatic systems [2]. The permissible limit of Cr(VI) in potable water is 0.05 mg L^{-1} [3,4]. Hence, the reduction of Cr (VI) level to the permissible limit (<0.5 mg L^{-1}) in the Cr(VI)-containing effluents is inevitable before being discharged into the environment.

The usual forms of phosphorus found in wastewaters include orthophosphate, polyphosphate and organic phosphate while the main aqueous species of Cr(VI) in wastewaters are CrO_4^{2-} ($pH > 6.5$) and $Cr_2O_7^{2-}/HCrO_4^-$ ($pH < 6.5$) [5]. A variety of physical-, chemical- and biological-based remediation processes for oxyanions of P(V) and Cr(VI) have been developed during the last few decades and adopted in practice depending on the nature of species present and composition of the wastewaters. The adsorption method using a variety of synthetic and natural adsorbents is still considered as one of the simple and effective processes among others and also covers a large number of studies in recent years [6–10].

A wide variety of Al-based synthetic materials and naturally occurring minerals/wastes like aluminium hydroxide [11,12], aluminium oxide hydroxide [13], commercial alumina [14], synthetic boehmite [15], red mud [16,17], kaolinite [18], bauxite [19–21], fly ash [22], alunite [23], etc. for the removal of aqueous P(V) oxyanions and aluminium hydroxide [24], red mud [25], clays [26,27], bauxite [28,29], fly ash [30], etc. for the removal of Cr(VI) oxyanions have been used as adsorbents. Although bauxite minerals have been often used for adsorptive removal of these oxyanions, the use of bauxite as such or heat treated with relatively high titanium content has not been studied so far due to their limited location specific availability. Keeping the above in view and in sequel to our previous study on defluoridation of drinking water using titanium-rich bauxite (TRB) [31], the present work investigates its adsorption potential for the removal of P(V) and Cr (VI) oxyanions under varying experimental conditions. The effects of heat treatment on sorption properties of resulting products have also been studied.

2. Materials and methods

2.1. Adsorbent materials

A typical bauxite sample with reasonably high titanium content (TRB), collected from Jobhipat bauxite mines of Jharkhand, was used in this study. Characterisations of TRB by chemical, thermal (TG-DTA), spectral (XRD, FT-IR) and surface area analyses in addition to determination of points of zero charge (pH_{zpc}) were same as described in our previous study [31]. In order to see the effect of thermal treatment, the raw TRB was heated at different temperatures in air for 4 h using a tubular furnace with programmable temperature controller. The raw TRB calcined at 200, 300, 450, 600, 750 and 900˚C were named as TRB-200, TRB-300, TRB-450, TRB-600, TRB-750 and TRB-900, respectively.

2.2. Sorption and desorption experiments

Stock oxyanion solutions of P(V) (1,000 mgP L^{-1}), Cr(VI) (250 mgCr L^{-1}) were prepared by dissolving KH_2PO_4 and $K_2Cr_2O_7$ (Merck, GR) in distilled water. Working solutions were prepared by suitable dilution of stock solutions with distilled water as and when required for different experiments. Adsorption of P(V) and Cr(VI) oxyanions experiments was carried out by batch equilibrium method. For this, 50 ml of P(V) or Cr(VI) oxyanion solution at desired concentration was mixed with an appropriate amount of adsorbent in 100-mL stopper conical flasks. The adsorbate solution was adjusted to the desired pH by adding dilute NaOH or HNO_3; the volume of NaOH or HCl never exceeded 0.5 ml. The flasks were mechanically shaken (100 strokes/min) in a thermostated water shaker at 30.0 ± 0.2˚C. Adsorbate solution, withdrawn at regular intervals, was centrifuged and the concentrations of P (V) or Cr(VI) in supernatants were determined spectrophotometrically by standard methods using phospho-vanado-molybdate and 1,5-diphenylcarbazide reagents, respectively. The amount of P(V) or Cr(VI) adsorbed was determined from the following relationship:

$$Q_{eq} = (C_t - C_{eq})V/m \tag{1}$$

where Q_{eq}, C_t, C_{eq}, V and m represent the amount of P (V) or Cr(VI) adsorbed on the solid (mg g^{-1}), the initial concentration (mg L^{-1}), the final concentration (mg L^{-1}), volume of the solution (L) and amount of adsorbent (g), respectively. Among different heat-treated samples, TRB-450 showed the highest uptake of oxyanions. Hence, further optimisation under varying experimental parameters like contact time, pH (3–9), adsorbent amount (2.0–10.0 g L^{-1}), oxyanion concentration (10–50 mgCr or mgP L^{-1}), temperature (30–50˚C) and presence of commonly occurring interfering ions in between (10–50 mg L^{-1}) was carried out using TRB-450.

The desorption of adsorbed oxyanion was carried out by treating the 0.1 g P(V) or Cr(VI) loaded TRB-450 with 50 mL of distilled water. The pH of the solution was adjusted to different values using aqueous solutions of NaOH/HNO_3 and then mechanically stirred for 2 h at room temperature. The amount of P(V) or Cr(VI) oxyanions desorbed into the solution was determined by methods described previously. All the adsorption/desorption experiments were carried out at least in duplicate and the average values were reported or used to derive other parameters. The variation of experimental data from average values was within 3–4%.

3. Results and discussion

3.1. Physicochemical characterisation of adsorbents

The raw TRB primarily constitutes of Al_2O_3 (53.9 wt%), TiO_2 (12.9 wt%), Fe_2O_3 (5.76 wt%), SiO_2 (1.35 wt%), CaO (0.007 wt%) as the major components while Ni (48 ppm), Cr (210 ppm), Cu (210 ppm), Zn (100 ppm), Co (52 ppm) are present in traces [31]. In addition, a very high value of loss of ignition (LOI) at 900℃ (25.4 wt%) indicates the presence of substantial amount of water/structural water in TRB. Powder XRD pattern of raw TRB showed the characteristic peaks of gibbsite and anatase along with one or two low intensity peaks for goethite and boehmite. On calcination at 450℃, the characteristic peaks of gibbsite were disappeared due to its conversion to boehmite [31] while the characteristic peaks due to anatase practically remained unchanged on calcination up to 750℃. Thermogravimetric (TG-DTA) analyses also supported the above observations [31]. The pH_{zpc} values of the raw TRB are marginally increased on calcination and found in the range 7.05–7.20. BET surface areas of TRB, TRB-450 and TRB-750 are found to be 13.1, 63.7.0 and 52.1 $m^2 g^{-1}$, respectively, indicating a gradual increase of surface area with the increase of heat treatment up to ~450℃ and thereafter decreases on further increase of temperature.

3.2. Effect of heat treatment

Heat treatment is one of the several ways to activate naturally occurring minerals used for adsorption of different oxyanions [20,21,28,29]. Calcination at moderate temperatures invariably leads to an incremental effect on adsorption efficiency due to surface modification, structural transformation and loss of structural water molecules present in the form of water of crystallisation, hydration of oxides or hydroxyl groups. Since the raw TRB contains sizeable amount of structural water, it would be interesting to see its role on overall adsorption behaviour of TRB. The effect of heat treatment on adsorption of P(V) and Cr(VI) oxyanions by TRB samples is shown in Fig. 1 along with corresponding water loss and progressive increase of combined wt% in (Al + Fe + Ti) constituents for comparison. Similar to that observed in the case of fluoride adsorption [31], the overall P(V) and Cr(VI) oxyanion uptake is found to increase with increasing temperature of heat treatment, attains a maximum value with TRB-450 and then decreases on further increase of temperature. This increase in adsorption capacity may be attributed to simultaneous increase in combined wt% of active components due to dehydration, increase in adsorption active sites and conversion of mineral phase gibbsite to boehmite. At 450℃, 17% overall weight loss of TRB is observed with simultaneous increase of combined (Al + Fe + Ti) wt% by ~1.2 fold. At this temperature, the P(V) and Cr(VI) oxyanions uptake is, however, increased by 2.1 and 2.2 folds, respectively. Hence, the increase of wt% active components (Al + Fe + Ti) does not fully account the increase of P(V) and Cr(VI) oxyanion uptake. The other probable factors responsible for this increase may be attributed to (i) increase of adsorption active sites due to dehydration that results thin capillaries in the bauxite matrix (ii) progressive increase of surface area and (iii) conversion of mineral phase gibbsite to boehmite having higher adsorption capacity. Previous studies [20] also emphasised that the dehydration leading to an increase in specific surface area and porosity of heat-treated bauxite is the major factor responsible for enhanced oxyanion adsorption.

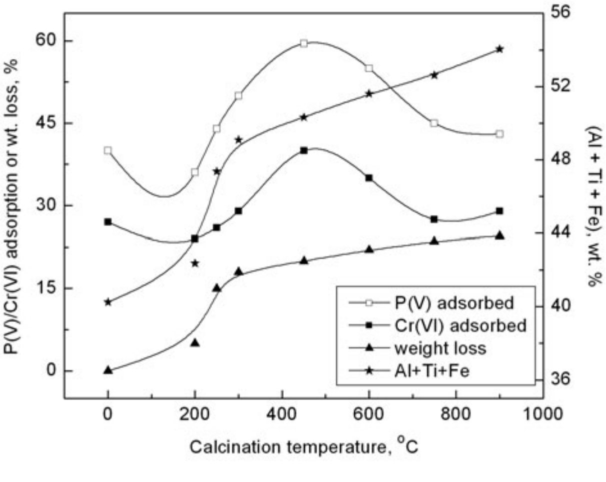

Fig. 1. Effect of calcination temperature on TRB for adsorption of P(V) and Cr(VI) oxyanions at pH 5.0 ± 0.2, adsorbent dose, 2 g L^{-1} and [adsorbate], 10 mg L^{-1}.

On further increase of calcination temperature, the uptake of both the oxyanions decreases primarily due to decrease in surface area and partial transformation of boehmite to γ-alumina [31] having lower adsorption capacity. As TRB-450 sample shows the highest uptake of both oxyanions, further optimisation was done with this sample only.

3.3. Contact time and adsorption kinetics

The adsorption of both the oxyanions under study is relatively rapid and more than 80–90% of total adsorption occurs in first 5–10 min followed by a slow process leading an equilibrium in 1 and 2 h for Cr(VI) and P(V), respectively (Fig. 2). Accordingly, all further experiments were carried out keeping these equilibrium time fixed. In order to understand the kinetics of adsorption process, the data at different temperatures were fitted to widely used Lagergren pseudo-first-order and pseudo-second-order rate equations. It is found that the adsorption data for both oxyanions are better fitted to Lagergren pseudo-second-order rate model yielding straight line plots between t/q_t vs. t with R^2 values 0.992–0.993. The pseudo-second-order rate constants (k_2) for P(V) oxyanion at 30, 40 and 50℃ are found to be 4.65×10^{-2}, 5.01×10^{-2} and 5.11×10^{-2} g mg^{-1} min^{-1}, respectively, in comparison with the values 0.112, 0.134 and 0.111 g mg^{-1} min^{-1} for Cr(VI) at 30, 40 and 50℃, respectively. Thus, the adsorption of Cr(VI) oxyanion is a relatively faster process than P(V) under identical conditions. The rate constants are in the range of those reported for adsorption of Cr(VI) oxyanions on naturally occurring bauxite (0.83 g mg^{-1} min^{-1} at 30℃) [29] or on activated alumina (0.0787 g mg^{-1} min^{-1} at 30℃) [7] but relatively lower than those reported for adsorption of P(V) oxyanion on naturally occurring bauxite (0.165 and 0.178 g mg^{-1} min^{-1} at 20 and 40℃, respectively) [21].

3.4. Effect of pH

The effect of initial pH on uptake of P(V) and Cr(VI) oxyanions is shown in Fig. 3. At fixed adsorbate concentration, the uptake of P(V) oxyanion increases with increase of pH up to ~5 followed by a sharp decrease on further increase of pH. A similar trend has also been reported earlier for its adsorption on various aluminium bearing adsorbents [18,19,32]. For instance, a pH increase from 4.3 to 9.0 remarkably decreased the P-adsorption capacity of alum sludge from 3.5 to 0.7 mgP g^{-1} [32]. On the other hand, a progressive decrease of Cr(VI) uptake with increase of pH is observed in the studied pH range which is consistent with those reported for its adsorption on alumina [33] or bauxite [21]. TRB is a complex mixture of different minerals with each having different pH$_{\text{pzc}}$ values. The different surface charges at a given pH leads to oxyanion adsorption over a wide pH range. The variations of oxyanion uptake may be explained considering the change of overall surface charge of TRB-450 and speciation of oxyanions as a function of pH.

Firstly, the overall surface charge of TRB-450 is positively charged at pH < 7 due to protonation but negatively charged at pH > 7 (pH$_{\text{pzc}}$ ~7). Depending on the pH of the medium, the hydroxylated adsorbent surface (S) can be either protonated and deprotonated

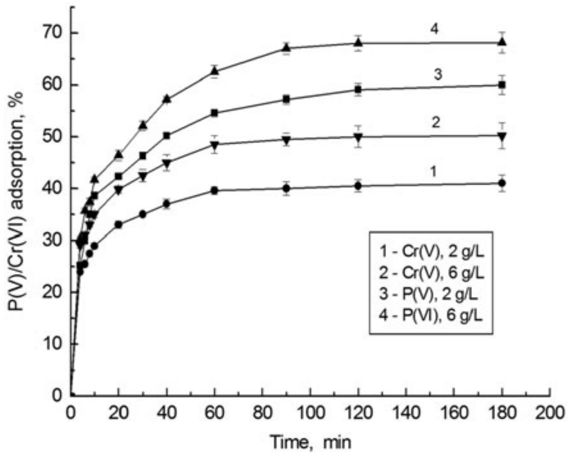

Fig. 2. Time variation adsorption of P(V) and Cr(VI) oxyanions on TRB-450 at different doses with fixed pH ~5.0 ± 0.2 and [adsorbate], 10 mg L^{-1}.

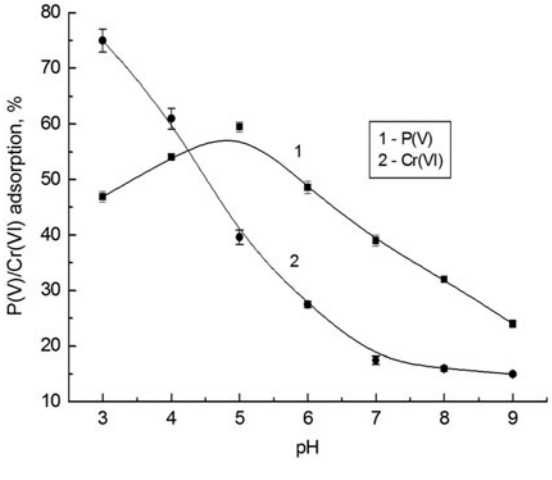

Fig. 3. Effect of pH on adsorption of P(V) and Cr(VI) oxyanions on TRB-450 with adsorbent dose, 2 g/L and [adsorbate], 10 mg L^{-1}.

according to Eqs. (2) and (3), respectively. If the number of protonated surface groups is more than the dissociated groups, the surface is positively charged and favours the anion adsorption.

$$\equiv\mathrm{SOH}_{(\mathrm{s})} + \mathrm{H}^{+}_{(\mathrm{aq})} \rightleftharpoons \equiv\mathrm{SOH}^{+}_{2(\mathrm{s})} \tag{2}$$

$$\equiv\mathrm{SOH}_{(\mathrm{s})} \rightleftharpoons \equiv\mathrm{SOH}^{-}_{(\mathrm{s})} + \mathrm{H}^{+}_{(\mathrm{aq})} \tag{3}$$

Secondly, $H_2PO_4^-$ and HPO_4^{2-} are the most abundant among different pH-dependent oxyanionic species of P(V) at $pH < 7.2$ and $7.2 < pH < 12$, respectively. At lower pH ($<pH_{pzc}$), the uptake of $H_2PO_4^-$ ion is favourable due to effective electrostatic attraction with positively charged surface of TRB-450. On the other hand, at higher pH ($>pH_{pzc}$), the electrostatic interaction between the most predominantly P(V) species (HPO_4^{2-}) and negatively charged TRB-450 is progressively decreased which in turn lowers the overall P(V) oxyanion uptake. In the case of Cr(VI), $HCrO_4^-$ is the predominant species in pH range 2.0–6.5 while CrO_4^{2-} is prevalent over other species at $pH > 6.5$. As expected, the electrostatic interaction of $HCrO_4^-$ ion with positively charged TRB surface favours higher uptake at lower pH. The uptake of Cr(VI) oxyanion decreases dramatically in pH range 7–9 due to less electrostatic interaction between negatively charged TRB at $pH > pH_{pzc}$ and CrO_4^{2-} ion which hinders the adsorption process. Further significant amounts of oxyanion adsorption at $pH > pH_{pzc}$ indicate that the adsorption is not fully controlled by simple Columbic interaction rather a ligand-exchange mechanism (outer or inner sphere) is also operative in the adsorption process as delineated in Eqs. (4) and (5). The involvement of $SOH^-_{(s)}$ group in the adsorption process is less likely. However, surface precipitation to a small extent, especially in case of phosphate as neutral species ($AlPO_4$, $FePO_4$), cannot be also ruled out.

$$\begin{aligned}&\equiv\mathrm{SOH}^{+}_{2(\mathrm{s})} + \mathrm{H_2PO}^{-}_{4(\mathrm{aq})}/\mathrm{HCrO}^{-}_{4(\mathrm{aq})} \rightleftharpoons\\ &\quad\equiv\mathrm{SOH}^{+}_{2} - \mathrm{H_2PO}^{-}_{4(\mathrm{s})}/\equiv\mathrm{SOH}^{+}_{2} - \mathrm{HCrO}^{-}_{4(\mathrm{s})}\end{aligned} \tag{4}$$

$$\begin{aligned}&\equiv\mathrm{SOH}^{+}_{2(\mathrm{s})} + \mathrm{H_2PO}^{-}_{4(\mathrm{aq})}/\mathrm{HCrO}^{-}_{4(\mathrm{aq})} \rightleftharpoons \equiv\mathrm{SH_2PO}_{4(\mathrm{s})}/\\ &\quad\equiv\mathrm{SHCrO}_{4(\mathrm{s})} + \mathrm{H_2O}_{(\mathrm{l})}\end{aligned} \tag{5}$$

3.5. Effect of adsorbent dose

Under identical conditions, the adsorption percentage of P(V) or Cr(VI) oxyanions is progressively increased with increase of adsorption dose from 2 to 10 mg L^{-1} but nearly complete removal of oxyanions (10 mgP and mgCr L^{-1}) is not achieved even at highest adsorbent dose. For instance, the percentage of P(V) oxyanion adsorption increases from 56 to 80 with increase of adsorbent dose from 2 to 10 g L^{-1} at the expense of decrease of P(V) uptake from 2.99 to 0.8 mgP g^{-1}. These values are comparable with those reported for calcined bauxite (2.95–0.98 mgP g^{-1}) [20] but relatively higher than those reported (2–0.95 mgP g^{-1}) for raw bauxite sample [21]. Under identical conditions, the adsorption of Cr(VI) oxyanion is, however, increased only from 40 to 56% for variation of adsorbent dose from 2 to 10 g L^{-1} with the decrease of Cr(VI) uptake from 2.0 to 0.56 mgCr g^{-1} and is consistent with the previous results (3.04–0.88 mgCr g^{-1} with increase of adsorbent dose from 20 to 100 g L^{-1} [29] and 2.2–0.19 mgCr g^{-1} with increase of adsorbent dose from 2.5 to 30 g L^{-1} [28]).

3.6. Adsorption isotherms

The effect of initial P(V) and Cr(VI) oxyanions concentration on their adsorption are presented in Fig. 4. As evident, the percentage of adsorption of both the oxyanions decreases with increase of initial concentrations and these adsorption data are fitted to two commonly used isotherms for adsorption of aqueous ions on hydr(oxide) surfaces. The adsorption parameter, derived from the least square fitting of adsorption data to the linearised forms of Langmuir (Eq. (6)) and Freundlich (Eq. (7)) adsorption isotherms, is collected in Table 1, along with those reported for relevant materials.

$$C_e/q_e = 1/(bQ_0) + C_e/Q_0 \tag{6}$$

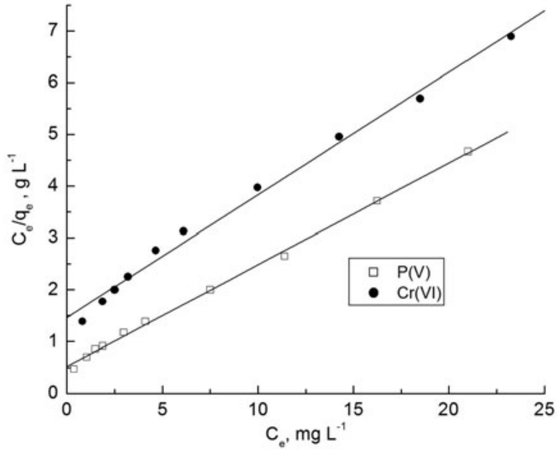

Fig. 4. Fitting of equilibrium adsorption data at varying initial P(V)/Cr(VI) concentrations (pH 5.0 ± 0.2 and TRB-450 dose, 2 g L^{-1}) to Langmuir equation.

Table 1
Adsorption parameters derived from Langmuir isotherm along with experimentally obtained maximum P(V)/Cr(VI) oxyanion uptake of aluminium-based materials/minerals

Sample description (Al_2O_3, wt%)	Surface area (m^2 g^{-1})	Initial [P(V)/Cr(VI)], mgP/Cr L^{-1}	pH	Max. P(V)/Cr(VI) uptake (Exptl.) (mgP/Cr g^{-1})	Langmuir Qo (mgP/Cr g^{-1})	Langmuir *b* (l/g)	Refs.
P(V) oxyanion							
Bauxite raw (56.91)	11.0 ± 0.5	10	4.45	0.673	–	–	[19]
Calcined[a]	86.0 ± 0.5	10	4.2	0.979	–	–	[20]
Bauxite		10	2.4	1.995	–	–	[21]
Fly ash (25.34)	0.53	80–130	11.5	71.87	–	–	[22]
AlO(OH) (69.5)	297	31	4	~42	–	–	[13]
Calcined alunite[b] (22.6)	148	5–200	5	106.6	118	0.115	[23]
Commercial alumina	200	10	6	~9.8	34.57	0.01	[14]
Kaolinite (33.8)	–	0–60	11.2	0.242	–	–	[18]
Alum sludge (~46)	–	5	4.3	–	3.5	–	[32]
TRB-450 (56.9)	63.7	10–50	5	2.9	5.102	0.377	This study
Cr(VI) oxyanion							
Activated bauxite[c] (56.9)	86.0 ± 0.5	2.5–50	2	0.3245	0.522	0.276	[28]
Calcined bauxite[d] (52.2)	167.53	10–30	3.8	0.245	2.021	0.2742	[29]
Activated alumina (93.1)	126	3–50	3	4.825	25.57	0.114	[7]
TRB-450 (56.9)	63.7	10–50	3	3.75	4.237	0.16	This study

[a] 600°C.
[b] 800°C.
[c] 600°C.
[d] 450°C.

$$\log q_e = 1/n(\log C_e) + \log K \tag{7}$$

where C_e is the equilibrium adsorbate concentration in solution (mg L^{-1}), q_e is the equilibrium adsorbate uptake per unit mass of adsorbent (mg g^{-1}), Q_0 is the maximum adsorption capacity (mg g^{-1}), and b is Langmuir constant (energy of adsorption); K and n are Freundlich constants and considered to be relative indicators of adsorption capacity and adsorption intensity, respectively. It is seen that the adsorption data for both the oxyanions are slightly better fitted to Langmuir isotherm ($R^2 = 0.99$) than Freundlich isotherm ($R^2 = 0.972$). The maximum adsorption capacities (Q_0) for P(V) and Cr(VI) oxyanions are found to be 5.1 mgP g^{-1} and 4.24 mg g^{-1}, respectively. It is worth noting that the Q_0 value in this study for Cr(VI) oxyanion are relatively higher than those reported for calcined bauxite (2.02 mgCr g^{-1}) [29] and (0.50 mg g^{-1}) [28]. The higher adsorption capacity of TRB may be partly attributed to the presence of higher titania content in the bauxite ore under study.

3.7. Effect of temperature

In order to get further insight into nature of adsorption process, the adsorption of oxyanions was studied at different temperatures keeping all other variables constant. It is seen that the percentage adsorption of P(V) oxyanion marginally increases (59–63.5%) with increase of temperature in the range 30–50°C and is consistent with that observed earlier [21]. On the other hand, the adsorption of Cr(VI) oxyanion increases (40–48%) with increase of temperature from 30 to 40°C and then decreases (48–38.3%) on further increase of temperature from 40 to 50°C indicating the optimum temperature for Cr(VI) adsorption is ~40°C. A similar trend has been reported for Cr(VI) adsorption on calcined bauxite [29] while Erdem et al. [28] have noted a progressive decrease of adsorption with increase of temperature from 20 to 50°C. The initial increase is presumably due to the requirement of activation energy for adsorption and the decrease in percentage of adsorption above 40°C may be due to the increase in desorption rate.

Thermodynamic parameters reflect the feasibility and spontaneous nature of an adsorption process and are derived using standard Eqs. (8)–(10).

$$K_C = C_s/C_e \tag{8}$$

$$\Delta G^\circ = -RT \ln K_c \tag{9}$$

$$\ln K_c = \Delta S^\circ/R - \Delta H^\circ/RT \tag{10}$$

where C_e is the equilibrium concentration in solution in mg L^{-1}, C_s is the equilibrium concentration on the adsorbent in mg L^{-1}, and K_c is the apparent equilibrium constant. ΔG°, ΔH° and ΔS° represent the change in free energy, standard enthalpy and standard entropy of adsorption. The thermodynamic parameters for P(V) adsorption were derived using Eqs. (8)–(10) and are collected in Table 2. For Cr(VI) adsorption, where K_c values do not increase regularly with increase of temperature, the values of K_c at 30 and 40°C were used to calculate the thermodynamic parameters using Eq. (11) and the values obtained are collected in Table 2.

$$\Delta H^\circ = R\{T_2T_1/(T_2 - T_1)\} \ln(K_{c2})/(K_{c1}) \tag{11}$$

K_{c1} and K_{c2} are the apparent equilibrium constants at temperatures T_1 and T_2, respectively.

The activation energy (E_a) for adsorption of P(V) oxyanion was determined by fitting the pseudo-second-order rate constant (k_2) to Arrhenius Eq. (12). For Cr(VI) adsorption, where k_2 values do not increase regularly with increase of temperature, the k_2 values at 30 and 40°C were used to calculate the E_a values using Eq. (13). The calculated E_a values for both oxyanions are given in Table 2.

$$\ln k_2 = -(E_a/RT) + \ln A \tag{12}$$

$$\ln(k_2/k_1) = E_a/R(1/T_1 - 1/T_2) \tag{13}$$

The negative values of ΔG° attribute to spontaneous nature of adsorption of both oxyanions [7,21,28,29]. More negative values of ΔG° with increase of temperature indicates that the adsorption of P(V) oxyanion is more favourable at higher temperature. In contrast, maximum negative value of ΔG° is found at 40°C in case of Cr(VI) oxyanion which becomes less negative on further increase of temperature. The positive ΔH° values suggest that adsorption of both P(V) and Cr(VI) oxyanions is endothermic. Moreover, ΔH° values within 1–20 kJ mol^{-1} further reveal that physisorption is much more favourable for adsorption of both the oxyanions. The positive ΔS° values indicate an increased randomness at the solid–solution interface of the adsorbent. The surface hydroxyl or hydrogen ions, displaced by the adsorbate species, gain more translational entropy than it is lost by the adsorbate molecules on adsorption and in turn increase the randomness of the system. The activation energy (E_a) of adsorption is found to be 5.74 and 13.63 kJ mol^{-1} for P(V) and Cr(VI) oxyanions, respectively. These values are slightly higher than those reported for P(V) adsorption by bauxite (3.13 kJ mol^{-1}) [18] and Cr(VI) adsorption on heat-treated bauxite (10.27 kJ mol^{-1}) [28].

Table 2
Thermodynamic parameters for the adsorption of P(V) and Cr(VI) oxyanion on TRB-450

Oxyanion	Temp. (°C)	K_C	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})	Ea (kJ mol^{-1})
P(V)	30	738	−16.33	7.94	81.1	5.74
	40	816	−17.44			
	50	877	−18.20			
		1,054[a]	−17.5[a]	6.943[a]		
Cr(VI)	30	355	−14.79	26.44	136.1	13.63
	40	496	−16.15			
	50	329	−15.56			
		48.5[b]	−9.78[b]			
			−23.24[c]		32[c]	10.27[c]
			3.26[d]	0.553[d]		

[a] At 30°C [21].
[b] At 30°C [7].
[c] At 30°C [28].
[d] At 30°C [29].

Table 3
Effect of some common competing anions in varying concentrations on per cent adsorption of P(V) and Cr(VI) oxyanions on TRB-450; Initial P(V) and Cr(IV) concentrations, 10 mg L^{-1}, pH 5.00 ± 0.2

	P(V) adsorbed (%)				Cr(VI) adsorbed (%)			
Competing ion, mg L^{-1}	Cl^-	NO_3^-	CO_3^{2-}	SO_4^{2-}	Cl^-	NO_3^-	CO_3^{2-}	SO_4^{2-}
0	60.0	60.0	60.0	60.0	40.0	40.0	40.0	40.0
10	60.0	59.8	51.3	49.5	40.0	40.0	39.1	38.2
20	–	59.2	45.4	41.3	39.8	–	36.1	35.2
30	59.4	58.2	42.4	39.4	39.5	–	34.2	29.3
40	59.0	–	41.5	35.4	39.3	39.2	30.2	25.3
50	58.5	56.0	40.5	30.1	–	–	29.1	20.2

3.8. Effect of coexisting anions

In reality, the contaminated water contains several other anions along with P(V) or Cr(VI) oxyanion which can equally compete in the adsorption process. The extent of interference primarily depends on the nature of the adsorbents used. The effect of some commonly occurring anions such as Cl^-, NO_3^-, CO_3^{2-} and SO_4^{2-} on adsorption of P(V) and Cr(VI) oxyanions is presented in Table 3. It is evident that the presence of Cl^- and NO_3^- up to 50 mg L^{-1} marginally effects the adsorption of P(V) or Cr(VI) oxyanion. Among SO_4^{2-} and CO_3^{2-}, the higher interference of SO_4^{2-} ion is presumably due to its relatively greater affinity with aluminium and titanium hydr(oxide) leading to blocking of active sites of TRB for adsorption of P(V) or Cr(VI) oxyanion.

3.9. Desorption/regeneration studies

The practical utility of adsorption process for the removal of different polluting ions from contaminated water lies in the desorption/regeneration ability of the adsorbent for reuse or safe disposal. In principle, an ideal desorption/regeneration process should restore the initial characteristics of adsorbent for its possible reuse. As the adsorption of P(V) and Cr(VI) oxyanion is pH dependent, desorption of these ions may be possible by controlling the pH of the eluent solution. The desorption profile of adsorbed oxyanions as a function of pH is presented in Fig. 5 which shows the release of ~6 to 75% and 8–70% adsorbed P(V) and Cr(VI) oxyanions, respectively, for an increase of pH from 5.0 to 10.0. The pH > 10 is deliberately avoided to check the dissolution of aluminium from TRB. This shows the adsorption of oxyanions on TRB-450 is not completely reversible and the adsorption process is controlled by both simple electrostatic interaction and ligand-exchange process. Further work is necessary to obtain a suitable regeneration process for the reuse of TRB.

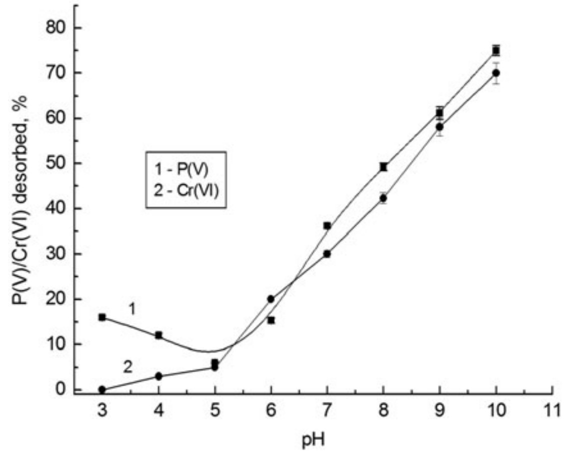

Fig. 5. Desorption of adsorbed P(V) and Cr(VI) oxyanions from TRB at different pHs.

4. Conclusions

This study demonstrated the potential of a selected high TRB mineral for adsorption of toxic oxyanions of P(V), and Cr(VI) by batch technique. The gibbsite content of raw bauxite is progressively decreased on heat treatment in between 100–450˚C due to its conversion to boehmite which is also evident from various physicochemical characterisations. TBR calcined at 450˚C (TRB-450) shows the maximum uptake of both the oxyanions which is strongly influenced on the pH of adsorbate solution. The adsorption data of both oxyanions are best fitted to Lagergren pseudo-second-order rate equation and to Langmuir adsorption isotherm model. The adsorption of both P(V) and Cr(VI) oxyanions is endothermic and is significantly affected by the presence of other oxyanions like SO_4^{2-} and CO_3^{2-}. The desorption of adsorbed P(V) and Cr(VI) is not completely reversible with increase of pH up to ~10. Considering the moderate adsorption capacity and low cost, the heat-treated TRB may be further exploited for its possible use as adsorbent for the removal of toxic anions by both batch adsorption and column methods.

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