

Surface modified alumina compact: A potential material for decontamination of trivalent and hexavalent chromium and growth inhibitor of microbes from water

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Abstract

A new hydrothermal approach has been investigated for synthesis of alumina which has been utilized for decontamination of trivalent and hexavalent chromium (Cr) as well as microbes from water. The heat treatment of aluminum nitrate and sucrose forms single phase γ -alumina compact of 318 m²/g surface area at 1100 °C. The carbon particles present in aluminum nitrate-sucrose system get oxidized as carbon dioxide. The removal efficiency of synthesized alumina has been compared with commercial alumina and studied as a function of pH, time and adsorbent dose. Interestingly, synthesized alumina have better removal efficiency than commercial one. The adsorption data was best fitted to Langmuir isotherm suggesting monolayer adsorption. The adsorption capacity of the proposed material was found to be 11.76 mg g⁻¹ and 11.9 mg g⁻¹ for Cr (III and VI) respectively, which is better than several inorganic materials reported. The proposed alumina also inhibits growth of several bacteria like *Bacillus cereus*, *Bacillus subtilis*, *Bacillus licheniformis*, *Staphylococcus aureus*, *Streptococcus pyogenes*, *Pseudomonas aeruginosa*, *Klebsiella pneumoniae*, *Serratia marcescens*, *Salmonella typhimurium* and *Proteus hauseri* upto 98%. The adsorption experiments were carried out in triplicate to get reproducible results. All experimental data for Cr removal has been reported with 95% confidence level (K=2). Copyright © 2017 VBRI Press.

Keywords: Alumina, chromium, adsorption, isotherm, microbes.

Introduction

The contamination of water by toxic species through discharge of industrial waste is a worldwide problem. Water pollution occurs when pollutants directly or indirectly discharged into water bodies without proper treatment. The consumption of water polluted by toxic heavy metals cause severe health problems. Chromium (Cr) is one such heavy metal which exists in various forms in environment such as metallic (zerovalent), trivalent and hexavalent. In water it mainly occurs in trivalent and hexavalent form. Cr (III) in trace amount serves as an essential nutrient for our body and plays vital role in secretion of insulin and fat metabolism. Cr (III) is found in the form of oxide, which is most stable state and found in several vegetables, grains, fruits, meats, yeast etc. Cr (VI) is mainly introduced into ground water when process solution from industries using Cr is discharged

without proper treatment. Cr (VI) is of particular concern because of its extreme toxicity to human health. Cr (VI) is more mobile and water soluble than Cr (III). The occurrence of trivalent and hexavalent Cr in water depends on water type, geographical location and the redox potential of water. The Cr (III) deficits may enhance diabetes symptoms, while long term exposure to Cr (III and VI) causes allergy, diarrhea, intestinal bleeding, cramps, paralysis [1, 2] and also affects vital organs. Cr (VI) is considered as carcinogenic [3], mutagenic [4] and teratogen [5].

The United State Environmental Protection Agency (US-EPA) and world health Organization (WHO) has set a maximum contamination level of Cr (VI) as 0.1 mg L⁻¹ and 0.05 mg L⁻¹ respectively in drinking water [6, 7]. To abate these problems, certain low cost methods without any side effects are pre-requisite. Many chemical methods

such as adsorption, chemical precipitation, electro flotation, ion-exchange, reverse osmosis etc. have been used for the removal of Cr [8-13]. Activated carbons, fly ash, slag, red mud, tea leaves, non-living ulva seaweed etc. materials have also been reported for the removal of toxic metals from contaminated water [14-17]. The Cr (VI) contaminated water can be purified either by direct removal of Cr (VI) or by reduction of Cr (VI) to Cr (III) followed by removal of Cr (III) [18].

The adsorption effect of alumina for several ionic species is already known [19-22]. In the proposed study, we have synthesized the alumina compact by new wet chemical route which involves controlled heat treatment of aluminum nitrate and sucrose mixture at 1100 °C. The adsorption efficiency of synthesized alumina has been investigated for removal of Cr (III and VI) as well as microbes. The microbes enter human being through water, soil, and food chain. Several infectious diseases in human beings like yellow fever, ringworm tuberculosis, plague, influenza, typhoid, hepatitis-A, amoebiasis, Taeniasis [23, 24] etc. are caused by consumption of microbes contaminated food and water. To inhibit the growth of microbes in water, several disinfectants are added to make it suitable for human consumption. Hence, the requirement of microbe free water is desired to mitigate microbial infection and to protect health of human beings. In literature several materials have been reported [25-30], out of which some removes only Cr, whereas some are suitable for microbe decontamination. But no one has reported same material for removal of both Cr (III and VI) as well as microbes. The proposed material have been utilized for inhibition growth of several microbes like *Bacillus cereus*, *Bacillus subtilis*, *Bacillus licheniformis*, *Staphylococcus aureus*, *Streptococcus pyogenes*, *Pseudomonas aeruginosa*, *Klebsiella pneumoniae*, *Serratia marcescens*, *Salmonella typhimurium* and *Proteus hauseri* etc. in contaminated water. The advantage of porous alumina for water purification is due to its high affinity to adsorb several toxic ions, its high surface area and low release of Al^{3+} into the solution. The removal efficiency of the synthesized alumina was studied as a function of pH, adsorbent dose, and contact time. Besides these Langmuir and Freundlich isotherm models have also been applied to study the adsorption behavior. The purified water can be used for drinking as well as several household applications.

Experimental

Materials and methods

The chemicals used for the synthesis of alumina and speciation study of Cr (III and VI) like aluminum nitrate, sucrose, hydrochloric acid and ammonium hydroxide, pyridine-2, 6-dicarboxylic acid (PDCA), diphenylcarbazine (DPC) were of analytical grade and procured from Merck chemicals. The synthesis of alumina has been done using Metrax India limited make muffle furnace workable upto 1450 °C. BDH make alumina marked as 'C' is commercially available and used to

compare its adsorption efficiency with synthesized alumina. The growth inhibition activity of alumina for microbes was analyzed using Shimadzu make spectrophotometer. The stock solution (1000 mg L^{-1}) of Cr (III) was prepared by dissolving required amount of chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$) in deionized (d.i.) water and Cr (VI) was prepared by dissolving required amount of potassium dichromate ($K_2Cr_2O_7$) in d.i. water. The synthesis, sample preparation, and dilution work have been carried out in d.i. water ($18.2\text{ M}\Omega\text{-cm}$ resistivity) prepared from USA make Millipore Milli-Q element water purification system. The reference standard solution of 1000 mg L^{-1} Cr (III) was used for calibration of instrument after subsequent dilutions. All experimental work was carried out in a laminar flow bench. The pipettes, beakers, volumetric flask were procured from Borosil Glass Works India Limited.

Synthesis of the Alumina powder

Two different alumina powders marked as 'A' and 'B' were synthesized using aluminum nitrate and sucrose in a ratio of 1:1 and 1:0.5 (w/w %), which was dissolved in de-ionized water. The mixture was then evaporated at 180 °C with constant stirring. The continuous heating causes foaming and puffing of mixture. On complete dehydration, brown fumes of NO_2 appear leaving behind voluminous organic based black slurry. The slurry was transferred to alumina crucible. The dried powder was then heated initially at 600 °C for 2 h and then at 1100 °C for 24 h.

Characterization

The crystallite size and phases of alumina powders 'A', 'B' and commercially available alumina 'C' were analyzed using Bruker make AXS D8 Advance powder X-ray diffractometer (XRD) with Diffrac^{plus} software. The morphology and elemental composition of the alumina powders were studied using LEO 440 scanning electron microscope (SEM) equipped with energy dispersive X-Ray Spectroscopy (EDS). The particle size of synthesized and commercial alumina was determined by dynamic light scattering (DLS) technique using Malvern, USA make Zetasizer, ZEN 3600 system. The surface area was calculated using Brunauer Emmett Teller (Quantachrome, model: Nove 2000c) in nitrogen environment at 77.4 K. The remaining concentration of Cr after adsorption was determined by Analytik Jena Germany make, Vario-6, Flame-Atomic Absorption Spectrophotometer (FAAS) using air (5.0 L min^{-1}) and acetylene (1.1 L min^{-1} fuel rich) at 357.9 nm wavelength. The speciation study of Cr (III and VI) was carried out using Ion Chromatograph system following EPA 218.6, 7199 methods and IC application note Metrohm AW IN6-0882-122008. Cr (III) was detected as its PDCA complex at 365 nm by pre-derivatizing it with eluent containing PDCA. Cr (VI) was detected by post column derivatization with DPC at 540 nm.

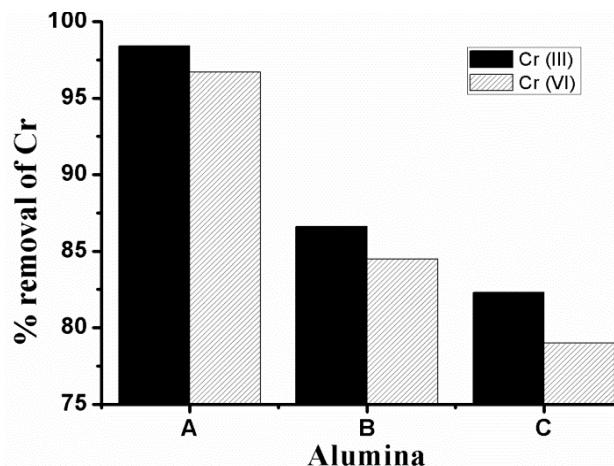


Fig. 1. Comparable removal efficiency of alumina 'A', 'B' and 'C' for Cr (III and VI).

Batch procedure for adsorption experiments

Batch adsorption experiments were carried out using both synthesized alumina ('A' and 'B') and commercial alumina ('C'). For this, known amount of alumina 'A', 'B', and 'C' were separately added in Cr (III and VI) solution having same volume and concentration (50 mL of 5 mg L⁻¹). The pH of each solution was kept around neutral. The solutions were then mixed and kept for 3 h. The alumina gets settled down and decanted solutions were analyzed by FAAS for left over concentration of Cr (III and VI). The adsorption capacity of alumina 'A', 'B' and 'C' for Cr (III and VI) was calculated using eq. (1), whereas percent removal of Cr (III and VI) by alumina was calculated using eq. (2).

$$\text{Adsorption capacity}(q_e) = \frac{(C_i - C_f)}{m} \times V \quad (1)$$

$$\% \text{ removal of Cr} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

where, 'C_i' and 'C_f' are the initial and final concentration of Cr (III and VI) solution (mg L⁻¹), V is the volume of solution used (L) and m is the weight of alumina (g). A bar chart representing comparable removal efficiency of alumina 'A', 'B' and 'C' for Cr (III and VI) has been presented in Fig. 1.

It was found that alumina 'A' have better removal efficiency than alumina 'B' and 'C'. So further adsorption

experiments were performed with alumina 'A' for different pH, adsorbent dose, contact time and initial concentration of Cr (III and VI) to study their effects on adsorption capacity of alumina A and to determine the maximum amount of Cr (III and VI) adsorbed.

Result and discussion

Characterization

The XRD patterns of alumina 'A', 'B' and 'C' were recorded in 2θ range from 20° to 80°. All the observed diffractions peaks correspond to γ-alumina (PDF # 50-0741, cubic Al₂O₃) confirming formation of a single-phase material in each case. The Crystallite size of above three alumina were estimated by using Scherer's equation [31] from the (440) peak.

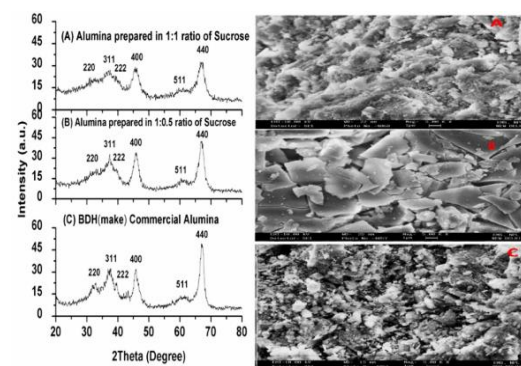


Fig. 2. XRD (left) and SEM (right) of synthesized alumina ('A' and 'B') and commercial alumina ('C').

The full width at half maxima (FWHM) of the peaks were estimated by fitting analytical profiles to the experimental profiles. Contribution of instrumental broadening to the FWHM was estimated by using XRD standard reference material (SRM 640c, silicon powder of NIST USA). The estimated crystallite sizes were found to be 39.2 Å, 48.6 Å, and 69.7 Å for alumina 'A', 'B' and 'C' respectively. The XRD of commercial and synthesized alumina powder has been given in Fig. 2 (left). The SEM micrographs of the commercial and synthesized alumina has been given in Fig. 2 (right). The microstructure analysis shows agglomerated nature of the particles. It has also been observed that agglomeration of the particle decreases with increase in concentration of hydrocarbon. For example, on increasing the ratio of sucrose from 0.5 to 1.0, the alumina converts into soft and

Table 1. Properties comparison of alumina 'A', 'B' and 'C'

Properties	Alumina, 'A'	Alumina, 'B'	Alumina, 'C'
Particle size (nm)	1426	1910	2927
Surface area (m ² /g)	318	308	258
Pore volume (cm ³ /g)	0.82	0.74	0.55
pH _{pzc}	7.70	7.37	6.59
Atomic % of oxygen	66.33	66.15	64.64
Atomic % of aluminum	33.67	33.85	35.36
Element % of oxygen	53.88	53.67	52.01
Element % of aluminum	46.12	46.33	47.99

spongy material (alumina 'A') as given in **Fig. 2A** (right). The material easily dispersed in water and removes maximum chromium and microbes, whereas alumina 'B' having lesser sucrose as given in **Fig 2B** (right) exists in hard flacks like form and removes less concentration of chromium as well as microbes than alumina 'A'.

The mean particle size for alumina 'A', 'B' and 'C' were found to be 1.4 μm , 1.9 μm and 2.9 μm respectively. The point zero charge (pH_{pzc}) of alumina was determined using rapid titration method [32]. The particle size, surface area, pore volume, pH_{pzc} and elemental compositions of all the three-alumina using EDS have been summarized in **Table 1**.

Effect of pH, adsorbent dose, time and concentration of chromium

The pH of the solution is a major controlling factor in the adsorption process. To study the effect of pH, a series of 50 mL solution of 5 mg L^{-1} concentration of Cr (III and VI) were taken in different sets. The pH of each set was adjusted between 2-12 range by 0.001M HCl and NaOH solution. In each set, 0.1 g of alumina 'A' was added and mixed thoroughly. The solutions were kept for 30 min and the decanted solution of each set was analyzed for left over concentration of Cr (III and VI) by FAAS. The effect of pH on removal of Cr (III and VI) has been given in **Fig. 3 (a)**. It has been observed that alumina 'A' has maximum adsorption capacity within 6.6-7.3 pH range.

The effect of adsorbent dose on removal efficiency of alumina 'A' was studied by varying the amount of adsorbent from 0.5 to 6 g L^{-1} , keeping other parameters constant like pH as 7, concentration of Cr (III and VI) as 5 mg L^{-1} and contact time as 30 min. The results are shown in **Fig. 3 (b)**. It has been observed that the removal efficiency of Cr (III and VI) increases with increasing adsorbent dose and maximum removal was occurred at 2 g L^{-1} , after which equilibrium was attained and a plateau has been observed. At this point, the amount of free ions and amount of ions bound to adsorbent remains constant even on addition of further adsorbent.

The removal of Cr (III and VI) was also studied as a function of time (2 min to 60 min) as given in **Fig. 3(c)** for 50 mL Cr (III and VI) solution having concentration 5 mg L^{-1} , at optimized adsorbent dose and pH. It has been observed that the removal of Cr (III and VI) increases with increasing time. Almost 95% of chromium (III and VI) have been removed within 20 min and maximum removal upto 99.8 % takes place within 35 min.

The effect of varying initial concentration of Cr (III and VI) from 1 to 25 mg L^{-1} on removal efficiency of alumina was studied at optimized pH, adsorbent dose and time as shown in **Fig. 3 (d)**. It has been found that % removal of Cr (III and VI) decreases with increasing initial concentration of Cr (III and VI). The decrease in % removal is due to fact that the adsorbent dose is fixed so active sites on adsorbent surface also gets fixed and could not increase in proportionate of Cr (III and VI) concentration. Thus % removal of Cr (III and VI)

decreases after adsorbing certain concentration by alumina.

Kinetics study

In order to analyze the adsorption process of Cr (III and VI) on alumina, pseudo first order and pseudo second order kinetic models were used. The linear pseudo first order and pseudo second order rate equations are represented by eq. (3) and (4) respectively.

$$\ln(q_m - q_t) = \ln q_e - K_1 t \quad (3)$$

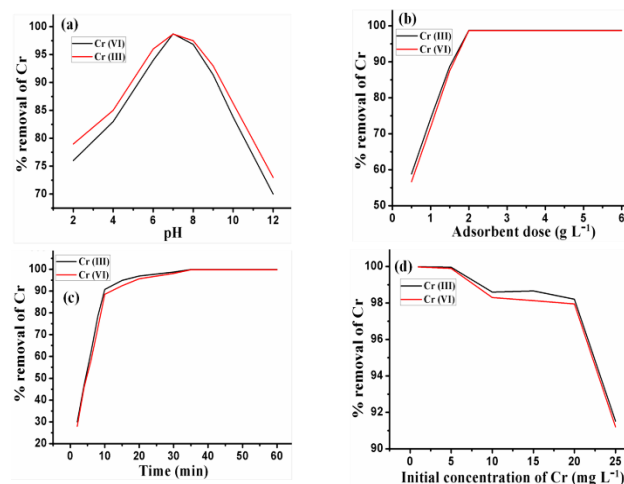


Fig. 3. Effect of (a) pH, (b) adsorbent dose (c) time and (d) concentration.

$$t / q_t = 1 / K_2 q_e^2 + t / q_e \quad (4)$$

where, q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amount of Cr adsorbed at equilibrium and at time t respectively, K_1 (min^{-1}) is the rate constant of pseudo first order rate equation and K_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of pseudo second order rate equation. The adsorption data from kinetics study was fitted to pseudo first order and pseudo second order rate equation. As per eq. (3) for first order kinetics, a linear curve was obtained on plotting ' $\ln(q_m - q_t)$ ' vs. ' t '. The value of K_1 for Cr (III and VI) calculated from the slope of above curve (**Fig. 4 (a and b)**) was found to be 0.154 and 0.139. The q_e calculated for Cr (III and VI) from intercept was found to be 1.874 mg g^{-1} and 1.941 mg g^{-1} respectively. Similarly, for second order kinetics (eq. 4), a linear curve was obtained on plotting ' t/q_t ' vs. ' t '. Slope and intercept of above curve (**Fig. 4 (c and d)**) gives the value of q_e and K_2 . The q_e calculated for Cr (III and VI) from slope was found to be 2.71 mg g^{-1} and 2.739 mg g^{-1} respectively. The value of K_2 calculated from intercept was found to be 0.105 and 0.089 for Cr (III and VI) respectively. The linear plots of pseudo first order and pseudo second order rate equations are shown in **Fig 4 (a-d)**.

From **Fig. 4**, it was found that that the adsorption data was best fitted to pseudo second order kinetic equation in comparison to pseudo first order kinetic equation based

on higher value of R^2 . It can be concluded that the rate of adsorption depends on concentration of adsorbate (Cr) and adsorbent (alumina).

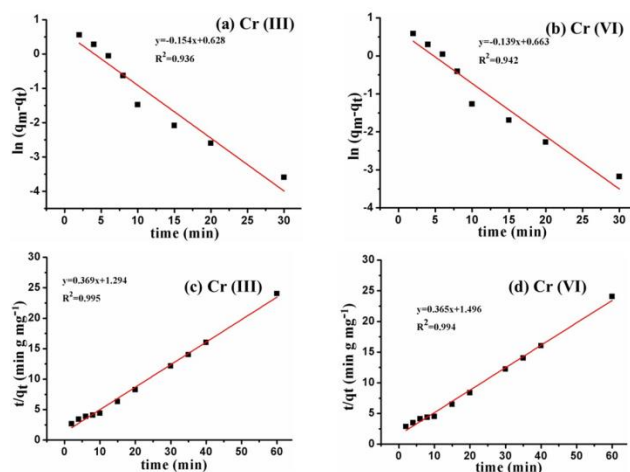


Fig. 4. (a and b) Pseudo first order, (c and d) pseudo second order kinetics for Cr (III and VI).

Adsorption isotherm study

The results of varying concentration of Cr (III and VI) adsorption on the surface of alumina were fitted to the Langmuir, Freundlich and Dubinin Raduskevich (D-R) isotherm model. The Langmuir isotherm suggests the monolayer adsorption on homogenous surface is expressed as,

$$C_f / q_e = C_f / q_m + 1/q_m K_L \quad (5)$$

where, C_f (mg L^{-1}) is the equilibrium concentration, q_e (mg g^{-1}) is the amount adsorbed at equilibrium; q_m (mg g^{-1}) and K_L (L mg^{-1}) are the Langmuir constants related to the capacity and energy of adsorption respectively. As per eq. (5), a linear curve was obtained on plotting ' C_f/q_e ' vs. ' C_f ', the slope and intercept of which gives the value of Langmuir constants q_m and K_L (Fig. 5 a and b). The q_m calculated from slope was found to be 11.764 mg g^{-1} and 11.904 mg g^{-1} for Cr (III and VI). Similarly, K_L calculated from intercept was found to be 14.166 L mg^{-1} and 10.5 L mg^{-1} for Cr (III and VI).

Fruendlich adsorption isotherm reveals the multilayer adsorption on the surface of adsorbent and indicates surface heterogeneity of adsorbent. The Freundlich isotherm is expressed as

$$\ln q_e = \ln K_F + 1/n \ln C_f \quad (6)$$

where, K_F [$\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$] and $1/n$ are temperature-dependent Freundlich constants related to adsorption capacity and adsorption intensity respectively; C_f (mg L^{-1}) is the equilibrium concentration and q_e (mg g^{-1}) is the amount adsorbed at equilibrium. By plotting ' $\ln q_e$ ' vs. ' $\ln C_f$ ' the value of K_F and $1/n$ for Cr (III and VI) can be obtained from the slope and intercept of the graph

(Fig. 5 c and d). The value of $1/n$ obtained from slope was found to be 0.305 and 0.346 for Cr (III and VI). Similarly, K_F obtained from intercept for Cr (III and VI) was found to be 11.067 and 10.764 respectively.

D-R isotherm suggests the adsorption mechanism of adsorbate over adsorbent and estimate energy of adsorption. The D-R isotherm is expressed as,

$$\ln q_e = \ln q_m - K \xi^2 \quad (7)$$

where, q_e (mg g^{-1}) is the equilibrium adsorption capacity, q_m (mg g^{-1}) is the maximum adsorption capacity, K is a constant related to adsorption energy and ξ is the polanyi potential.

$$\xi = RT \ln(1 + 1/C_f) \quad (8)$$

where, R ($=8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) is universal gas constant, T is the temperature in Kelvin and C_f (mg g^{-1}) is the equilibrium concentration. As per eq. (7), a linear curve was obtained on plotting ' $\ln q_e$ ' vs. ' ξ^2 ', the slope and intercept of which gives the value of K and q_m (Fig. 5 e and f). The value of K obtained from slope was found to be $5.498 \times 10^{-9} \text{ mol}^2 \text{ kJ}^{-2}$ and $7.139 \times 10^{-9} \text{ mol}^2 \text{ kJ}^{-2}$ for Cr (III and VI).

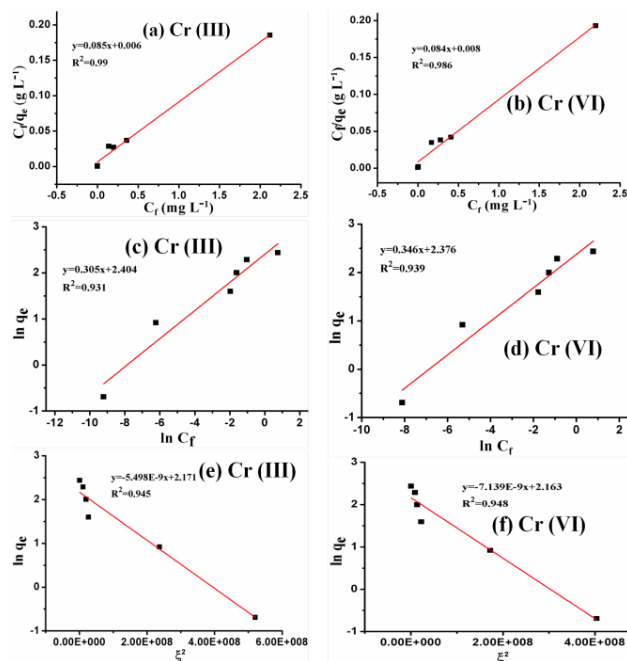


Fig. 5. (a and b) Langmuir, (c and d) Freundlich and (e and f) D-R isotherm for Cr (III and VI).

Similarly, q_m obtained from intercept for Cr (III and VI) was found to be 8.767 mg g^{-1} and 8.697 mg g^{-1} respectively. The constant K gives the mean free energy of adsorption (E) when one molecule of adsorbate (Cr) is transferred from solution to the surface of solid (adsorbent).

$$E = (-2K)^{-0.5} \quad (9)$$

The value of E is useful in predicting the type of adsorption. If its value is less than 8 kJ mol^{-1} , then physical adsorption occurs and if it is above 8 kJ mol^{-1} , chemical adsorption takes place. The value of E for Cr (III and VI) was calculated to be $9536.359 \text{ kJ mol}^{-1}$ and $8368.861 \text{ kJ mol}^{-1}$ respectively. The linear plots of Langmuir, Freundlich and D-R isotherms for Cr (III and VI) are shown in **Fig. 5 (a-f)**.

The Langmuir isotherm model was found to be most suitable based on higher value of R^2 . The adsorption capacity calculated from Langmuir isotherm was found to be 11.764 mg g^{-1} and 11.904 mg g^{-1} for Cr (III and VI) which is in agreement with experimental adsorption capacity i. e. 11.44 mg g^{-1} and 11.40 mg g^{-1} respectively. Thus, it can be concluded that adsorption of Cr (III and VI) takes place as a monolayer coverage on the homogenous surface of alumina.

Desorption and reusability study

Desorption and reusability study was performed to find out the practical utility of proposed alumina. In desorption study alumina utilized in first experiment was separated by centrifuge system and dried at 105°C . Then utilized alumina was then ultrasonically stirred in fresh DI water at three different pH (4.5, 6.5 and 8.5) for 15 minutes. The decanted solution was tested once again for leaching out concentration of Cr (III) and (VI). It was observed that maximum desorption of Cr (III) and (VI) occurred at pH 8.5. The separated alumina at pH 8.5 was then reused for further adsorption of Cr (III) and (VI) upto 3 cycles following same adsorption and desorption process. It was found that in the first cycle the proposed alumina removed 92.5% of Cr, which further reduces upto 74.5% in next cycle.

Proposed mechanism for adsorption of Cr (III and VI) by alumina

The maximum adsorption of Cr (III and VI) takes place at pH 7 at which Cr (III) exists as $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and Cr (VI) exists in CrO_4^{2-} , whereas alumina exists in neutral form. The Al of alumina interacts with the O of both the Cr species through surface complexation mechanism which is responsible for adsorption of Cr (III and VI) by alumina. The possible mechanism for interaction of Cr (III and VI) by alumina is shown in **Fig. 6 (a and b)**.

Removal of Cr (III and VI) species

The limit of detection (LOD) and limit of quantification (LOQ) were calculated from blank by averaging the signal of all blanks. The uptake of Cr (III and VI) species at initial concentration of 5 mg L^{-1} and 1 mg L^{-1} respectively was studied using 2 g L^{-1} alumina for 3 h at pH 7. However, as the limit of detection of Cr (III and VI) is less than 1 mg L^{-1} and $40 \text{ }\mu\text{g L}^{-1}$ concentrations respectively.

So in order to quantify the trace level of these species, additional 1 mg L^{-1} Cr (III) and $40 \text{ }\mu\text{g L}^{-1}$ Cr (VI) was added into the filtrate. A strong signal was observed for Cr (III) at 3.5-4.5 minute and a prominent peak of Cr (VI) was observed at 7.5-8.5 min. The concentration of Cr (VI) in the filtrate was obtained by subtracting the concentration of added Cr (VI) in the filtrate. It was found that 1.1 mg L^{-1} of Cr (III) and $22 \text{ }\mu\text{g L}^{-1}$ of Cr (VI) were left over in the filtrate. About 99% of Cr (III) and almost entire Cr (VI) have been removed at the optimum conditions.

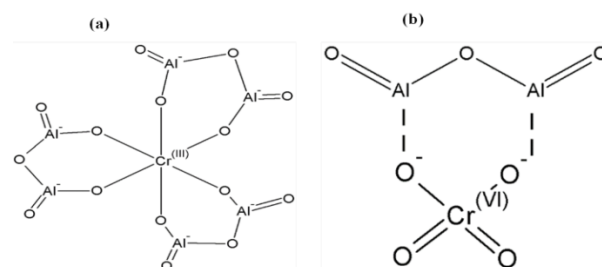


Fig. 6. Mechanism of interaction of alumina with (a) Cr (III) and (b) Cr (VI).

Interference studies

The efficiency of fixed quantity of alumina (0.25 g) for Cr removal has been checked in presence of several ions. 50 ml of 5 mg L^{-1} Cr standard solutions were taken in separate beakers. To these solutions $1\text{-}5 \text{ mg L}^{-1}$ of several ions commonly present in water (like Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Pb^{2+} , Zn^{2+} , Cu^{2+} , Fe^{2+} and As^{3+}) were added at optimized conditions. The water was mixed thoroughly and kept for 40 min . The decanted solutions were tested for remaining concentration of Cr by FAAS. It has been observed that 5 mg L^{-1} of Cr can be removed in presence of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} individually and these ions do not interfere in Cr removal. Whereas 1 mg L^{-1} of As^{3+} and Pb^{2+} also gets adsorbed over the surface of alumina along with Cr. But on further increasing concentration of as upto 5 mg L^{-1} for same amount of alumina, the more amount of As^{3+} get adsorbed preferentially over the surface of alumina compact. The Zn^{2+} and Fe^{2+} do not interfere in Cr removal upto 2 mg L^{-1} , but on further increasing concentration of Zn^{2+} and Fe^{2+} the efficiency of alumina decreases $10\text{-}15\%$ which reveals that Zn^{2+} and Fe^{2+} may also get adsorbed over the surface of alumina. The decrease in Cr removal efficiency of alumina may be due to the consumption of alumina by other ionic species. To confirm this, the amount of alumina was increased upto 0.5 g for same concentration. In this case, more than 99.6% of Cr along with other species like As^{3+} , Pb^{2+} , Zn^{2+} and Fe^{2+} have been removed.

Comparison of proposed adsorbent with various adsorbents in literature

The proposed alumina was also compared with other inorganic based adsorbents cited in the literature as given in **Table 2** which reveals that proposed alumina has better

efficiency for Cr (III and VI) removal in comparison to other materials. The alumina works in neutral pH. While some materials which shows better efficiency than proposed alumina works in acidic pH range. For functioning of such materials, the pH of water have to be adjusted prior to treatment, whereas there is no need to adjust the pH of water for functioning of proposed material.

Table 2. Comparison of various adsorbents.

Adsorbent	Adsorption capacity (mg g ⁻¹)	pH	References
Kaolinite	6.1	4.6	[33]
Red clay	1.3	4 - 6.5	[34]
Silica	1.5	2-4	[35]
Zeolite HDTMA	39.47	6	[36]
Clinoptilolite-ODA	54	3.0	[37]
HDTMA-Modified Zeolites	0.763	7	[38]
Cowlesite			
Clinoptilolite HDTMA	0.844	7	[38]
HDTMA-Modified Zeolites	0.103	7	[39]
Alumina compact	11.7-11.9	7	Proposed study

Data accuracy

The adsorption experiments were carried out in triplicate to attain the reproducible results with an error less than 1%. Various equipment and apparatus like weighing balance, volumetric flask, pipettes etc. used in the Cr removal experiment were calibrated prior to use by CSIR-National Physical Laboratory-India (National Metrology Institute of India) following international standard procedure and protocol. The stock solutions were prepared gravimetrically and the respective certified reference standards were used for calibration of FAAS. The process blank was also done and considered for final calculations. All the data was reported with 95% confidence level (k=2).

Antimicrobial activity

It is essential to purify the water contaminated by microbes to protect human beings and environment. Worldwide several efforts have been made to find out new innovative safe processes, which are eco-friendly, low cost and suitable to ecological balance. In the present investigation, the microbial growth inhibition activity of proposed alumina was carried out by turbidimetric analysis using Shimadzu make spectrophotometer and plate count method by growing in nutrient broth, Hi-media.

Antimicrobial activity of alumina (100-500 µg mL⁻¹) was tested against gram positive *Bacillus cereus* (ATCC 14579), *Bacillus subtilis* (MTCC 6051), *Bacillus*

licheniformis (ATCC 14580), *Staphylococcus aureus* (ATCC 25923), *Streptococcus pyogenes* (ATCC 19615) and gram negative *Pseudomonas aeruginosa* (ATCC 14207), *Klebsiella pneumoniae* (ATCC 13883), *Serratia marcescens* (ATCC 8100), *Salmonella typhimurium* (ATCC 14028) and *Proteus hauseri* (ATCC 13315) strains with the help of spectrophotometric method. The nutrient broth was inoculated with loopful of bacteria and incubated at 37 °C, 120 round per minute for 12-14 h for mother culture. 100 µL of mother culture (O.D. 0.8 or cfu 1×10⁸ mL⁻¹) was inoculated aseptically in fresh nutrient broth with different concentration of alumina and incubated at 37 °C overnight. After incubation, their antimicrobial effect has been observed by measuring the optical density (absorbance) at 660 nm in comparison to control of each strain. The Percent inhibition was calculated using eq. (10)

$$\% \text{ Inhibition} = \frac{(O.D. \text{ control} - O.D. \text{ test})}{O.D. \text{ test}} \times 100 \quad (10)$$

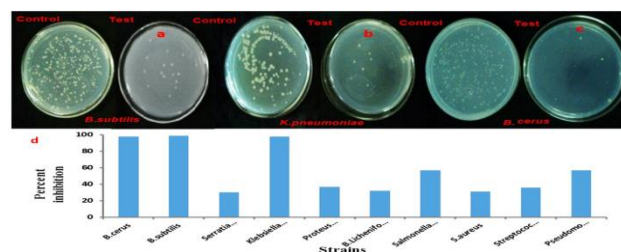


Fig. 7. Effect of alumina nanoparticles on (a) *B. subtilis*, (b) *K. pneumoniae* and (c) *B. cereus* bacteria respectively and (d) Inhibition growth of various microbes.

Fig. 7 (a), (b) and (c) shows the effect of alumina microparticles on some representative microbes like, *B. Subtilis*, *K.pneumoniae* and *B.cerus*, while **Fig. 7 (d)** shows graphical representation of growth inhibition of various gram positive and gram negative bacteria. From the experiments, it has been observed that growth of the microbes reduced with increase in concentration of alumina. It has been found that 400 µg mL⁻¹ of alumina concentration inhibits 98-99% growth of *B. cereus*, *B. subtilis*, *Klebsiella pneumonia*, 57% inhibition in *Salmonella typhimurium* and *Pseudomonas aeruginosa*, whereas only 30% to 37% inhibition in case of *Serratia marcescens*, *proteus hauseri*, *B. Licheniformis*, *Staphylococcus aureus* and *Streptococcus pyogenes*.

The inhibitory effect of alumina might be attributed to the electrostatic interaction between positive charged surface on the alumina microparticles around neutral pH and negatively charged bacterial cells along with hydrophobic interactions and polymer bridging which may lead to the adhesion of nanoparticles on the bacterial surfaces [40]. The close interaction inflicts oxidative stress inside the bacterial cell and consequent damage to proteins, membranes, and DNA leading to cell death. Further, cell wall disruption and drastic antimicrobial action may be due to formation of reactive oxygen species by alumina particles.

Conclusion

The synthesized alumina is found to be an effective adsorbent for the removal of Cr (III and VI) from aqueous solution. The adsorption capacity of the proposed alumina was found to be better than the several inorganic based materials reported in the literature. The adsorption effect of alumina for Cr (III and VI) removal has been done at optimize pH in presence of several ionic species. The removal was found to be strongly dependent on pH, adsorbent dose, and contact time. The adsorption process of Cr (III and VI) was studied with isotherm models and the adsorption data was best fitted to Langmuir isotherm model due to the monolayer adsorption on the porous alumina surface. The synthesized alumina also shows good antimicrobial activity with possibility to inhibit 30-99 % growth of different microbes. The commercial alumina has also been tested for the same experiments and was found ineffective. But more studies are needed to optimize the system from regeneration point of view to investigate the economic aspects and to confirm the applicability of proposed alumina under real condition such as industrial effluent management.

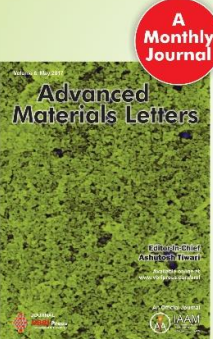
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