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The use of functionalized aerogels as a low level chromium scavenger

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ABSTRACT

This paper communicates synthesis of aminopropyl functionalized aerogel by grafting 3-aminopropyltrimethoxy silane (APTMS) onto the surface of nano sol–gel silica by post synthetic grafting procedure. The physico-chemical behavior of the grafted silica is investigated by SEM, XRD, FTIR and TGA techniques. The BET surface area analysis technique is used for the determination of the surface area, total pore volume and pore diameter. The effectiveness of chromium removal was systematically monitored as a function of the pH of the medium, agitation time, Cr(III) ions concentration and functionalized silica dosage. The chromium uptake followed Freundlich, Langmuir and D–R isotherm models and sorption capacity computed from the Langmuir model is 1.67 mmol g^{-1}. The effect of temperature on sorption is also checked and various thermodynamic parameters like ΔH, ΔS, and ΔG are calculated and discussed. Regeneration studies show that the sorbent is reusable. The effect of interfering cations and anions is also investigated.

1. Introduction

Silica aerogels are highly porous structures and have been the subject of extensive research since their discovery [1]. The attractive properties of these materials like high specific surface area, low density and greater chemical, mechanical and thermal stability make them potential candidates in many practical applications like catalysis and sorption [2–6]. The unique property of these materials is their three dimensional network system accessible to sorbed molecules through their highly porous structure. Sol–gel is a commonly used synthesis technique for these materials and has received tremendous technical and commercial importance [7–9]. Mesoporous silica's with tailored functional groups are excellent nanostructures, which combine the inherent properties of inorganic backbone and the specific selectivity of organic functional groups. The surface functionalization of these structures can be accomplished by incorporating chemical groups into their porous three dimensional networks directly [10,11] or through post grafting procedure. Functionalized aerogel is a potential candidate for the cleaning of the low level impurities from aqueous, petrochemicals and gaseous media. Modified silica have attracted special attention in different areas like metal ions preconcentration, ion exchange, biotechnology, catalysis and green chemistry [12–16].

Literature reveals that amine functionalized silica is extensively studied in solid phase extraction [17] either covalently attached to silica or simply impregnated on silica surface for heavy metals like Cu(II), Cd(II), Hg(II) Co(II), Ni(II), Zn(II) and Pb(II) [18–26]. The complexation ability of amine bearing silica is also utilized for the voltammetric detection of trace Cu(II) [27].

Chromium compounds are used in several industrial applications such as leather tanning, metal finishing, pigment manufacturing and electroplating [28]. Exposure to chromium compounds causes a wide range of clinical/health disorders [29]. Cr(VI) is more toxic than Cr(III), where the leather industry produces a large amount of Cr(III) rich waste that could be potentially oxidized to Cr(VI). Therefore, removal/recovery of Cr(III) from the industrial wastewater is important from both environmental and economic point of view. It may reduce the risk of polluting environment while the recovered Cr(III) can be reused [30,31].

The removal of chromium ions from water is a serious issue in Pakistan. There is a large number of tanneries, where leather is the second largest export earning and has 5% share in the GDP. The tanneries in Pakistan discharge their wastes untreated to water bodies. The literature reveals that aminated silica is an effective sorbent for the separation of various heavy metals, but very little is reported about its efficiency in the separation/preconcentration of chromium. In this work amine functionalized aerogels are synthesized and their efficiency for the removal/preconcentration of Cr(III) ions is investigated.

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2. Experimental

2.1. Reagents and chemicals

All the reagents in this study were of analytical grade and used without any further purification. The buffer solution (1–8) with an ionic strength of 10 mmol was prepared using an appropriate volumes of solutions of KCl and HCl (pH 1–2), sodium acetate and acetic acid (pH 3–6), Boric acid and sodium hydroxide (pH 7–8).

The radiotracer ^{51}Cr was prepared by irradiating spec pure metal in swimming pool type research reactor PARR-1 of PINSTECH at a neutron flux of 7×10^{13} s^{-1} for 12 h. The irradiated metal was dissolved in concentrated HCl and the acid was removed by repeated evaporation with distilled water and diluted to 5.0 cm^3 having a concentration of 2.94×10^{-2} M and used as stock solution. The radiochemical purity of the tracer was checked by using 25 cm^3 Ge(Li) detector coupled with a 4 k series of 85 Canberra, USA multichannel analyzer.

2.2. Synthesis of APTMS functionalized nano aerogels

Nano particles were prepared using sol–gel method as reported earlier [32]. For $-NH_2$ functionalization, 2.5 ml of silylating agent 3-aminopropyltrimethoxy silane (APTMS) was drop wise added to 2.5 g of calcined nano silica particles and was refluxed in 50 ml of n-hexane for 6 h in a conical flask. The synthesis scheme is presented in Fig. 1. The resulting residue was filtered, washed with deionized water and n-hexane and kept overnight at room temperature.

2.3. Chromium sequestration

Chromium uptake was investigated in batch experiments using radiotracer technique at room temperature (25 ± 1 °C) unless described. A known quantity of radiotracer was added to a 5 cm^3 solution of an electrolyte of specific pH, in 30 cm^3 glass vial and activity was mixed uniformly. 1 cm^3 solution was taken out from this solution for gross gamma counts (A_0). A_0 is considered as initial concentration of Cr (III) solution. The remaining solution was equilibrated with a known amount of functionalized aerogel for a specific period of time and shaked. Gross gamma-ray detection was made on a Tennelec, USA counting assembly equipped with a 25 cm^3 NaI(Tl) crystal and shaking was performed on wrist action mechanical shaker (Griffin UK). After shaking, the solution was centrifuged for at least 5 min and 1 cm^3 of the aliquot was taken out for radio assay (A_e). A_e is the equilibrium concentration of chromium removed. % Sorption was calculated by using the following relationship:

$$\% \text{ Sorption} = \frac{A_0 - A_e}{A_e} \times 100 \quad (1)$$

2.4. Determination of point of zero charge (pH_{zpc})

The point of zero charge (pH_{zpc}) of the APTMS functionalized aerogels was determined by the solid addition method. 50 ml of 0.1 M $NaNO_3$ solution was transferred into series of 100 ml stoppered conical flasks. The initial pH values were adjusted between 2 and 9 by adding either dilute 0.1 M HCl or 0.1 M NaOH. 0.2 g of the adsorbent was added to each flask, and the flasks were tightly capped. After periodical shaking of 24 h, the final pH values of the supernatant solutions were noted. The initial pH values were plotted verses final pH values (Fig. 2). The intersection point of curve was 7 representing the pH_{zpc} of the APTMS functionalized aerogels.

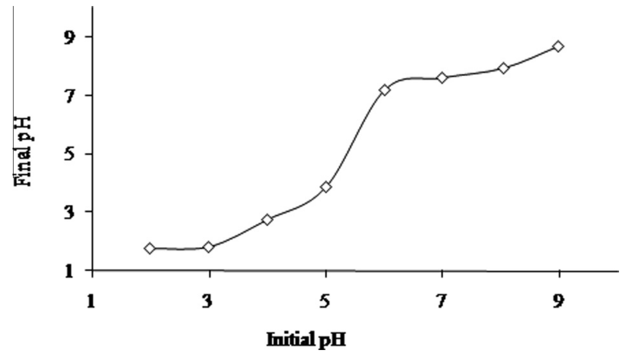

Fig. 2. Point of zero charge (pHzpc) of APTMS functionalized aerogels.

3. Results and discussions

3.1. Characterization of the sorbent

X-ray diffraction (XRD) pattern of virgin aerogel and APTMS modified aerogels are shown in Fig. 3. The broad horn peak at 22° is the distinguishing silica peak and represents amorphous nature of silica [33] and broad peaks at small edges are due to the absence of long-range crystallographic order. After calcinations at 900 °C the original broad peak at 2θ, 22° was reduced and intense peaks appeared at 22°, 29°, 32°, 36° showing some changes in the crystalline domain of silica.

After functionalization with APTMS the XRD peak position remained the same and silica retained its amorphous nature showing that functionalization process does not affect material's morphology.

The synthesized material is porous in nature having a high surface area of 920 m^2/g, pore volume of 0.96 cm^3/g and a pore diameter of 4.17 nm calculated from Brunauer–Emmett–Teller (BET) equation using N_2 sorption experiments. The high surface area is an important factor for immobilization of amine and other organic molecules.

The scanning electron microscope (SEM) images of virgin (left) and functionalized nano aerogel (right) are presented in Fig. 4. This reveals that particles maintain their spherical morphologies following the chelation of organic ligand. This suggests that the ligand anchoring is a chemical process and does not affect the surface morphology of the material. The surface of the silica aerogel is fine-tuned with desired functional groups without disturbing the basic morphology of the parent aerogels.

Fourier transform infrared (FTIR) spectroscopy is used for the identification of the functional groups present in the synthesized sorbents using KBr pellets technique (Fig. 5). Absorption band at

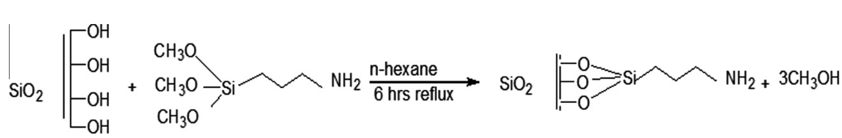

Fig. 1. Synthesis scheme for preparing APTMS functionalized aerogels.