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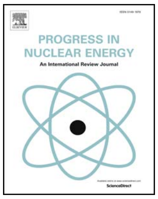

Complexation of Hg(II) ions with a functionalized adsorbent: A thermodynamic and kinetic approach

Zarshad Ali[a], Rashid Ahmad[b,*], Aslam Khan[c], Bushra Adalata[a]

[a] Department of Chemistry, Hazara University, Mansehra, Pakistan
[b] Department of Chemistry, University of Malakand, Chakdara, Dir (L), Pakistan
[c] Chemistry Division, PINSTECH, PO Nilore, Islamabad, Pakistan

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ABSTRACT

A new functionalized hybrid adsorbent is prepared by covalent grafting of thiosemicarbazide to the silica surface for the abatement of environmental mercury. The material was characterized using spectral techniques like SEM, TGA, FTIR, EDX and BET surface area analysis. The EDX images showed that the chelating ligand was successfully grafted on the surface. The material is analyzed as Hg(II) extractant by using radiotracer in batch experiments. Maximum adsorption capacity for the adsorbent is about 4.83 mg g^{-1} at pH 7, pHzpc 6.5 and equilibration time of 30 min. The kinetics are best described by Pseudo second order kinetic model ($R^2 > 0.99$). The equilibrium adsorption data are modeled with Langmuir, D-R and Freundlich isotherms. The adsorption capacity (0.05 mmol g^{-1}) calculated from Freundlich model is in agreement with the experimental results (0.023 mmol g^{-1}). Freundlich isotherm predicted heterogeneous nature of the sorbent surface and infinite surface coverage. The adsorption process of mercury is endothermic ($\Delta H = 27.53\ J\ K^{-1}\ mol^{-1}$), favorable ($\Delta S = 106.13\ J\ K^{-1}\ mol^{-1}$) and spontaneous ($\Delta G = -\ 3695.83\ J\ mol^{-1}$) in nature, as suggested by thermodynamic investigations.

1. Introduction

During the last few decades, significant progress has been made in separation sciences and new classes of non-carbonaceous and carbonaceous materials i.e. zeolites, activated carbons, clays, alumina, molecular sieves, biomasses, resins and polymeric hydrogels (Yamazaki et al., 2015; Arima et al., 2016; Dąbrowski, 2001; Samiey et al., 2014; Hara et al., 2016) have been utilized for, removal of heavy metals from drinking water, industrial wastewaters and nuclear waste management. All these adsorbents had some merits and demerits. Majority of them suffered from their intrinsic limitations i.e. low uptake, high regeneration costs, poor selectivities, low mechanical and chemical stabilities (Nagarale et al., 2006). Due to these shortcomings, industrial scientists were forced to look for new materials as suitable alternatives to these adsorbents to reduce processing costs and energy requirements. Industries continued to struggle for environmentally benign and safer methods for the cleaning of hazardous wastes. To serve this need, silica was thought to be a promising candidate due to large surface area, mechanical and chemical stability, rapid attainment of equilibrium and possible reuse (Cestari et al., 2006). The silica surface decorated with organic-functional groups has received attention of the researchers in numerous applications such as radiotracer adsorption, ion-exchange operations, bio-technology, catalysis and green chemical process (Kikuchi et al., 2005; Lee et al., 2003; Raj et al., 2013; Ali et al., 2014).

Mercury is a potent toxicant which causes a number of enzymatic and neurological disorders (Carter et al., 2014) in humans and animals and is therefore of great environmental significance. Over the years researchers have adopted different procedures for the treatment of contaminated wastewaters and industrial effluents. However, they have limited applications due to the heavy wastes production (solvent extraction and chemical coagulation), high costs (zeolites), lower efficiencies (clays, activated carbons), lower selectivities and poor mechanical stabilities (ion exchange resins). Some of them are energy intensive (evaporation and electrolysis) require costly installations (reverse osmosis and filtration) and are environmentally unviable due to production of sludge. (Samiey et al., 2014). One of the strategy (Walcarius and Mercier, 2010) for the treatment of mercury containing wastes is to covalently bind mercury on a solid surface grafted with organic functional groups. Hard and soft (Lewis) acids and bases (HSAB) concept (Pearson, 1988), predicts that sulphur has a strong chemical affinity for mercury and thio-functionalized silica's (Billinge et al., 2005; Olkhovyk and Jaroniec, 2005; Aguado et al., 2008) have

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* Corresponding author.
E-mail address: rashidahmad@uom.edu.pk (R. Ahmad).

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been investigated for mercury remediation. These surface modified adsorbents selectively adsorb and trap mercury ions from the medium and have significant adsorption capabilities.

For all these essential features of functionalized sorbents, in this paper, we deal with the synthesis of a functionalized adsorbent, prepared by covalent grafting of a chelating ligand, thiosemicarbazide to the silica surface. Silica nanospheres were prepared under basic condition by sol–gel method using hexadecyltrimethylammoniumbromide (CTAB) as template and tetraethoxysilane (TEOS) as the silica source. The incorporation of amine functional groups into mesoporous silica was achieved by a liquid phase grafting method. The adsorbent was characterized by spectral techniques like SEM, TGA, FTIR, EDX and BET surface area analysis and was employed for the sequestration of mercury in a batch mode using radiotracer technique. The adsorption chemistry of mercury was exhaustively investigated on the surface of the modified adsorbent. A number of adsorption parameters such as effect of pH, agitation time, temperature and concentration of mercury were investigated systematically to ensure the best possible use of the adsorbent as mercury scavenger. Langmuir and Freundlich isotherms were applied to the experimental equilibrium data to explain the adsorption mechanism. The synthesized adsorbent can selectively adsorb and clean Hg(II) ions from aqueous solutions. Thiosemicarbazide is an important complexing ligand with S – N donor groups used in biological and pharmacological applications previously (Hassanien et al., 2008; El-Asmy et al., 2010) and can form complexes with various metals including mercury.

2. Experimental

2.1. Chemical reagents used

All the chemicals purchased for this study were of analytical grade and used without any pretreatment. TEOS (tetraethylorthosilicate 97%), added as a silica source, CTAB (cetyl-trimethylammonium- bromide) used as a surfactant and coupling agent APTMS (3-aminopropyltrimethoxy silane) were all supplied by Sigma-Aldrich. Thiosemicarbazide (TSC) was supplied by East-man (Germany). The radiotracer of mercury (^{203}Hg) was prepared by neutron radiation of spectroscopically pure mercury oxide. A fixed quantity (17 mg) of the metal was sealed in a fusion tube and then coated with aluminum. The aluminum coated capsule containing the metal was subjected to a constant neutron flux of 7×10^{13} n cm^{-2} s^{-1} for 12 h. The radiotracer was kept for cooling and after one week; it was dissolved in conc. hydrochloric acid. Then diluted with de-ionized water and heated to dryness, to remove the excess of acid. The process of dilution and evaporation was repeated three times, till the complete evaporation of the acid and 10.0 mL stock solution (3.1 mg mL^{-1}) was prepared finally. The ^{203}Hg radiotracer purity was confirmed by germanium lithium (Ge/Li) sensor attached to a multichannel analyzer, Canberra-85, (USA).

A number of buffers (pH 1 to 8) were prepared by mixing some acids and their salts, such as HCl/KCl for pH 1–2, CH_3CO_2H/CH_3CO_2Na for pH 3–6, H_3BO_3/NaOH for pH 7–8. Metrohm-605 model pH meter was used for adjusting solution pH. Pyrex glass vials (30 mL) provided with polythene screw caps were used for shaking and centrifugation of solutions. A Tennelec counting assembly with NaI (Tl) detector (USA) was used for gross gamma counts.

2.2. Synthesis of silica and grafting of the chelating ligand

Nano spheres of silica and 3-aminopropyltrimethoxysilane (3-APTMS) modified silica were synthesized as reported elsewhere (Heidari et al., 2009). Based on this method, Silica nano spheres were prepared under basic condition by sol–gel method using hexadecyltrimethylammoniumbromide (CTAB) as template and tetraethoxysilane (TEOS) as the silica source. For grafting, 5.0 g thiosemicarbazide was mixed with deionized water (50.0 mL) in a flask fitted with a condenser and placed on hot plate. Formaldehyde (30 mL of 37%) was injected drop wise to the reaction mixture and then refluxed for 1 h. There after pre-synthesized APTMS functionalized silica (10 g) and 50 mL methanol was introduced to the mixture and again refluxed for another 1/2 h. The grafted silica formed was filtered and washed with de-ionized water, methanol, and ethanol and calcined in tube furnace at 45 °C for 12 h.

2.3. Mercury ions sequestration experiments

Hg(II) ions adsorption was carried out in batch operation mode, using ^{203}Hg radiotracer. The experiments were conducted at 25 ± 1°C or described otherwise and optimized conditions i.e.20 mg of adsorbent, mercury concentration of 3.69×10^{-2} mmol l^{-1}, 30 min agitation time, 10 min centrifugation time at pH 5 in 5.0 mL of total volume. Mercury% adsorption was measured as

$$\% \text{ Sorption of Hg(II)} = A_0 - A_e / A_0 \tag{1}$$

Where A_o is the initial concentration and A_e is the equilibrium concentration of Hg(II).

K_D, the distribution coefficient was calculated as

$$K_D = \frac{\text{amount of Hg(II)}\mathit{adsorbed}}{\mathit{amount\ of\ Hg(II) in\ solution}} \times \frac{\text{volume of solution(V)}}{\text{mass of adsorbent(W)}} = \left(\frac{\text{mL}}{\text{g}}\right) \tag{2}$$

2.4. Zero point charge (pHzpc) determination

pHzpc is a key characteristic of the material, which describes the point where the electrical charge on its surface is zero. The pHzpc value of the functionalized sorbent was measured by solid addition technique. 25.0 mL of NaNO3 solution (0.1 M) was transferred to 100 mL air tight volumetric flasks and 25.0 mg of the dry sorbent was added to each flask. Dilute HCl/NaOH (0.1 M) was added to these flasks to adjust the pH and agitated for 24 h and pH of the supernatant solution was determined. The difference between final and initial pH was plotted verses initial pH (Fig. 1). The curve intersected the zero line at pH 6.5, which was taken as the point zero charge (pHzpc) of adsorbent.

3. Results and discussions

3.1. Essential features of adsorbent

Morphological characteristics of adsorbent such as surface area, pore volume and pore size distribution were measured by Brunauer–Emmet–Teller (BET) analysis, using nitrogen sorption/desorption experiments. These investigations suggested that the functionalized adsorbent is porous with a surface area of around 922 m^{2}g,$^{-1}$ pore

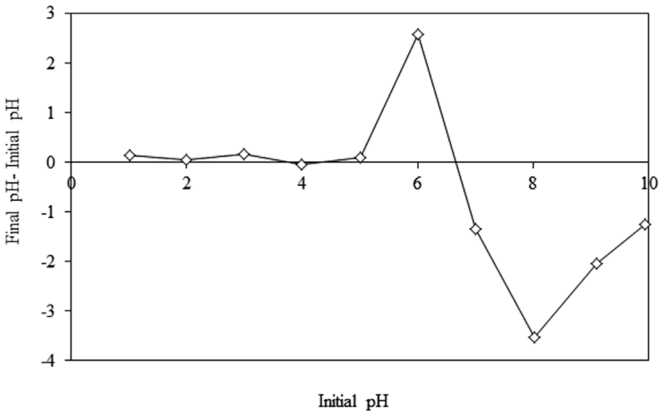

Fig. 1. Point zero charge (pHzpc) of adsorbent.