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Magnetic silica nanoparticles for the removal of Pb^{+2} from water

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Zero valent iron impregnated silica nanoparticles (Fe^0/n-SiO_2) were synthesized using sol-gel process followed by supercritical drying, wet impregnation and hydrogen reduction. The synthesized nanoparticles were characterized by nitrogen Brunauer–Emmett–Teller (N_2-BET), Scanning Electron Microscopy, Transmission Electron Microscopy, Scanning Electron Microscopy with Energy-Dispersive X-ray spectroscopy, Vibrating Sample Magnetometer and X-ray diffraction techniques. Prepared samples were found to be magnetic with ultra-low density (0.048 g/mL) and high surface area (422 m^2/g). Prepared samples were evaluated for adsorptive removal of Pb^{+2} (5, 10, 25 and 50 ppm) from contaminated water. Results indicated that the adsorption of Pb^{+2} was faster at lower concentrations (5 and 10 ppm) as > 80 % of Pb^{+2} was removed within 480 minutes. At higher concentrations, the adsorption was slower, and the removal efficiency of 51.24 and 21.78 % were observed for 25 and 50 ppm Pb^{+2} respectively, whereas for bare SiO_2 nanoparticles, it was 39.64 and 14.04 %.

Keywords: Fe^0/n-SiO_2, Pb^{+2}, removal capacity, removal percentage, pH enhancement.

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1. Introduction

Lead (Pb^{+2}) is one of the most common and hazardous inorganic water pollutants. A huge amount of Pb^{+2} is introduced daily in water streams in the form of wastewater from industries such as battery and paint manufacturers. Lead-containing pipes used in water supply systems are also responsible for the water contamination [1]. It has been proved that Pb^{+2} is non-biodegradable and produces poisonous effects on living beings. In the human body, it can accumulate in kidneys, bones, muscles and may cause of anaemia, irritability, dizziness, renal weakness and cancer [2]. The World Health Organization (WHO) has set permissible limit for Pb^{+2} as 0.010 mg/L in potable water. To reduce the threats of Pb^{+2} poisoning, many water treatment techniques have been developed for the removal of Pb^{+2} from water. Common treatment methods for Pb^{+2} removal from water are chemical precipitation, ion exchange, electro-flotation, membrane filtration and reverse osmosis [3]. All of these methods have some commercial and operational limitations, therefore, it is essential to develop new technologies having low cost and high Pb^{+2} removal efficiencies. There has been intense interest in the utilization of nanoparticles for the purification of Pb^{+2}-contaminated water. Due to their small size and high specific surface area, nanoparticles possess a wide range of reactive sites to adsorb environmental contaminants [4]. Various nanoparticles have been previously reported for the removal of Pb^{+2} from water. Nano zero valent iron (Fe^0) has been found as one of the most successful nano-adsorbent for the removal of Pb^{+2} from contaminated water [5]. Although Fe^0 has been proved to be an efficient adsorbent of Pb^{+2}, it also has some drawbacks. It is highly unstable and is readily oxidized with atmospheric oxygen and water. Furthermore, Fe^0 nanoparticles also aggregate with time and due to these drawbacks the available binding sites and reactivity of these nanoparticles become reduced. To overcome or minimize these drawbacks, Fe^0 nanoparticles have been loaded or impregnated on solid supports. Various composites of Fe^0 nanoparticles supported/ impregnated clays, zeolites, etc. have been previously reported for the removal of Pb^{+2} from contaminated water [6]. Silica based solid supports (zeolites, MCM-41 and SBA-15) have been found most suitable matrices among all supporting materials for the impregnation of Fe^0 nanoparticles [7]. Previous attempts to disperse Fe^0 nanoparticles over silica were limited to SBA-15 and MCM-41. In the present work, we report the synthesis of high surface area and low density Fe^0 impregnated silica nanoparticles (Fe^0/n-SiO_2) and their application for the removal of Pb^{+2} from contaminated water.

2. Preparation and characterization of Fe^0/n-SiO_2

The synthesis of Fe^0/n-SiO_2 was carried out by a two-step procedure, in the first step, SiO_2 nanoparticles (n-SiO_2) were synthesized by the sol-gel procedure followed by supercritical drying of liquid gel to aerogel at 265 °C [8]. In the second step, the synthesized SiO_2 particles were impregnated with solution of $FeCl_3$ in methanol containing 8.0 % w/w of Fe. The material was dried and subjected to reduction under H_2 gas at 600 °C for 3 – 4 h. This resulted in magnetic silica nanoparticles having 7.2 % Fe^0 (determined by Atomic Absorption Spectrophotomer).

Detailed characterization of n-SiO_2 has been reported in our previous communications [8, 9], herein the characterization of impregnated system, i.e., Fe^0/n-SiO_2 has been discussed. Nitrogen adsorption-desorption isotherm of Fe^0/n-SiO_2 showed type IV pattern, which indicated that all particles have mesoporous characteristics. The appearance of H3 hysteresis loop also signified the presence of slit shaped pores in nanoparticles and wide pore size distributions [10]. Fe^0/n-SiO_2 showed BET surface area as 422 m^2/g. The BJH pore size distribution curve of Fe^0/n-SiO_2 indicated pore maxima for micropores and mesopores at 18 and 200 Å respectively. Fe^0/n-SiO_2 was found to possess low density (0.048 g/mL) and low moisture content (0.56 %). The X-ray diffraction (XRD) pattern of Fe^0/n-SiO_2 (Fig. 1) was matched from reported literature. It displayed the characteristic peak at 44.83 °, which indicated the presence of iron predominantly in the zero valency state, diffraction peaks at 44.83 ° (110), 64.99 ° (200) and 82.45 ° (211) confirmed that the Fe^0 is in bcc (body-centered cubic) phase (JCPDS 00-006-0696). Moreover broad hump at 21.56 ° indicated the presence of amorphous hydrated silica [11].

Scanning Electron Microscope (SEM) image of Fe^0/n-SiO_2 (Fig. 2) displayed its dendritic texture in which all nanoparticles aggregated and depicted huge porosity. Scanning Electron Microscope with Energy-Dispersive X-ray spectroscope (SEM-EDX) data of Fe^0/n-SiO_2 indicated around 7.2 % loading of Fe^0 with uniform distribution on the silica nanoparticles (Fig. 3). Transmission Electron Microscope (TEM) image of Fe^0/n-SiO_2 indicated the spherical shape of prepared nanoparticles (Fig. 2-inset). The particle diameter Fe^0/n-SiO_2 was observed in between 7 to 32 nm (maximum particles were of 17 nm). The magnetic properties of Fe^0/n-SiO_2 were examined using Vibrating Sample Magnetometer (VSM) analysis. The appearance of hysteresis loop indicated the value of saturation magnetization (M_s) ~ 4.409 emu/g with a high coercivity (H_c) of 121.7 Oe. The sample showed higher coercivity and lower saturation magnetization in comparison to bulk iron (H_c=0.9 Oe, M_s=220 emu/g), which is indicative of iron particles in nanometer size range [12], furthermore, these impregnated nanoparticles also showed magnetic attraction. Characterization data of Fe^0/n-SiO_2 supported the formation of low density magnetic zero-valent iron loaded SiO_2 nanoparticles. Characterization data also suggested that the surface area, bulk density and moisture content of bare n-SiO_2 were decreased, whereas particle size of n-SiO_2 increased after impregnation with Fe^0 (Table 1).

TABLE 1. Characteristics of bare n-SiO_2 and Fe^0 impregnated n-SiO_2

Adsorbent	Bulk density (g/ml)	Moisture content (%)	Surface area (m^2/g)	Particle size range (nm)	Particle shape
n-SiO_2	0.035	0.80	628	3 – 25	Spherical
Fe^0/n-SiO_2	0.048	0.56	422	7 – 32	Spherical

3. Absorptive removal of Pb^{+2} using prepared nanoparticles

Prepared nanoparticles of n-SiO_2 and Fe^0/n-SiO_2 were examined to remove Pb^{+2} from water. The experiments were carried out at four different Pb^{+2} concentrations, viz, 5, 10, 25 and 50 ppm. Adsorptive removal studies were performed at a dose level of 1 mg/mL (nanomaterial/ Pb^{+2} solution). 100 mg of Fe^0/n-SiO_2 was taken separately in 100 mL Pb^{+2} solutions of different concentrations. All samples were shaken continuously in rotatory shaker at the speed of 200 rpm. After shaking for fixed time periods, 2 mL sample was taken out, centrifuged and separated. Additionally, the Pb^{+2} concentrations were determined using an Atomic Absorption Spectrophotometer. Results indicated > 80 % removal of Pb^{+2} by both the adsorbents within 360 min for 5 ppm Pb^{+2}. As the concentration of Pb^{+2} varied from 5 to 50 ppm the adsorption potential of n-SiO_2 and Fe^0/n-SiO_2 decreased from 100 to 14.04 % and 100 to 21.78 % respectively within 2880 min (Fig. 4 and 5).

The change in pH during the kinetics experiments was also measured because of its importance in controlling the removal of Pb^{+2}.

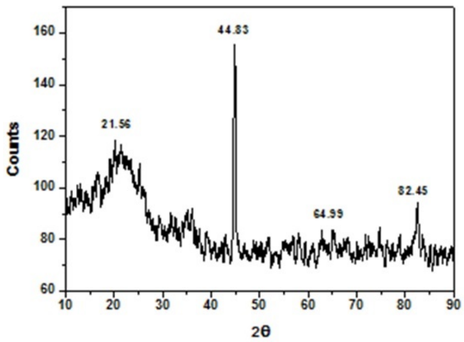


FIG. 1. XRD pattern of Fe^0/n-SiO_2

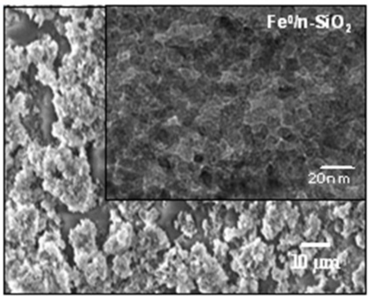
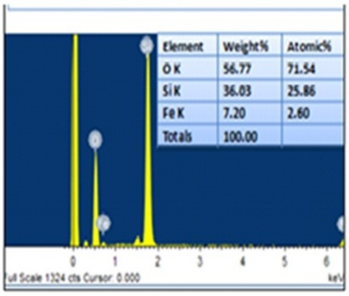


FIG. 2. SEM & TEM (inset) images



Element	Weight%	Atomic%
O K	56.77	71.54
Si K	36.03	25.86
Fe K	7.20	2.60
Totals	100.00	

FIG. 3. SEM-EDX of Fe^0/n-SiO_2

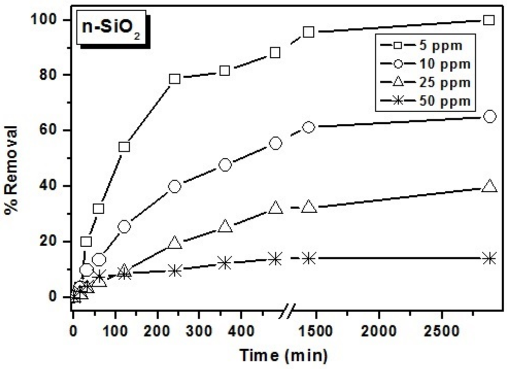


FIG. 4. Removal of Pb^{+2} by n-SiO_2

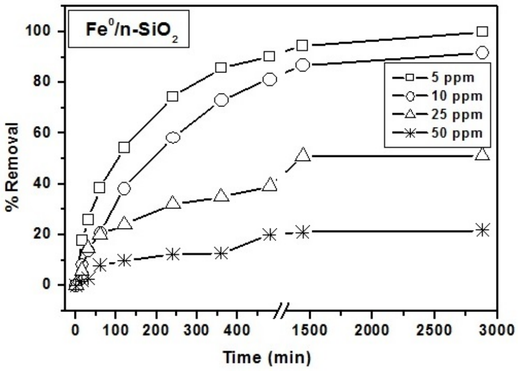


FIG. 5. Removal of Pb^{+2} by Fe^0/n-SiO_2

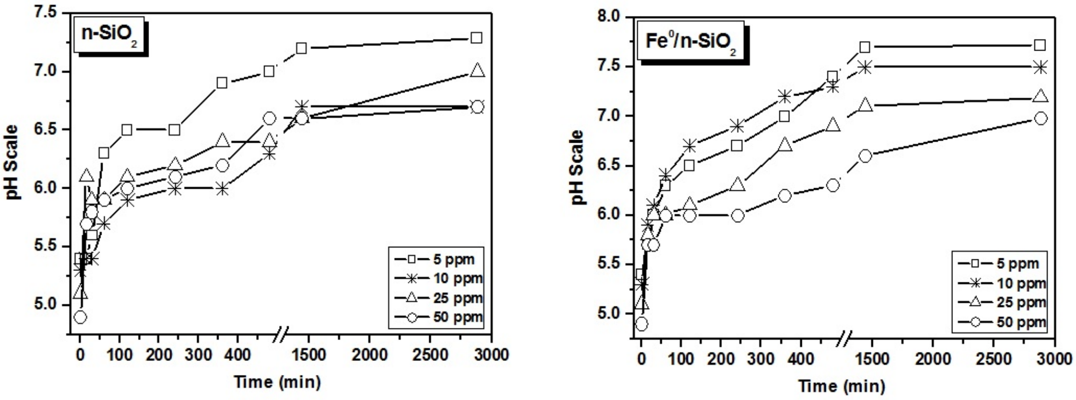


FIG. 6. Change in pH by the both adsorbents during Pb^{+2} removal

Considerable change in pH for n-SiO_2 and Fe^0/n-SiO_2 was observed during the Pb^{+2} removal studies (Fig. 6). The maximum hike in pH for n-SiO_2 and Fe^0/n-SiO_2 was measured as 7.29 and 7.72 respectively (initial pH was 5.4). The increase in pH of medium by zero valent iron impregnated nano adsorbents was due to the formation of iron oxide/hydroxides on oxidation in aqueous medium. The removal kinetics also affected at higher pH as Pb^{+2} got precipitated to Pb^0, PbO, $Pb(OH)_2$, etc. [9] at this pH. Here, it was also noticeable that the removal of Pb^{+2} increased with gradual increase of the medium's pH, which may be due to the protonation/deprotonation of the hydroxyl species on the surface of the nanoparticles. Overall studies indicated Fe^0/n-SiO_2 system as a promising material for the removal of Pb^{+2} from contaminated water.

4. Conclusion

Magnetic nanoparticles of Fe^0/n-SiO_2 with high surface area and low density were prepared using the sol-gel method followed by wet impregnation technique and hydrogen reduction. The synthesized nano-composite and bare SiO_2 nanoparticles were evaluated for adsorptive removal of Pb^{+2} from contaminated water. Although the surface area of n-SiO_2 was higher than Fe^0/n-SiO_2, yet it showed lower Pb^{+2} removal percentage. The pH enhancement (up to 7.72) by both adsorbents was also recorded during the removal studies. The results suggested that the removal of Pb^{+2} by both the adsorbents may be due to high surface area and also by the protonation/deprotonation of the hydroxyl species created on the surface of nanoparticles after reaction with water. Further work is going on to establish the specific mechanism for Pb^{+2} removal.

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