International Research Journal of Environment Sciences ISSN 2319–1414
Vol. **1(5),** 6-13, December **(2012)** *Int. Res. J. Environment Sci.*

Efficiency of Superparamagnetic Nano Iron Oxide loaded Poly (Acrylamide-co-Acrylic acid) Hydrogel in Uptaking Pb^{2+} Ions from Water

Tiwari Alka* and Sharma Neeraj
Department of Chemistry, Govt. V.Y.T. PG. Autonomous College, Durg, CG, INDIA

Available online at: www.isca.in
Received 10th October 2012, revised 19th October 2012, accepted 25th October 2012

Abstract

A novel adsorbent, superparamagnetic nano iron oxide loaded poly (acrylamide-co-acrylic acid) hydrogel (superparamagnetic PAA hydrogel), was employed for the removal of toxic lead ions from aqueous solution. The influence of pH, contact time, metal ion concentration, adsorbent dose and temperature on the sensitivity of the removal process was investigated. The synthesized copolymer was magnetized insitu and the size, structure and coating of magnetic nano particles were characterized by TEM, XRD and FTIR analysis respectively. The sorption data was analyzed and fitted to linearized adsorption isotherm of the Langmuir, Freundlich and Temkin equations respectively. This hydrogel has been found to be an efficient adsorbent for toxic Pb^{2+} *ions removal from water (>98% removal) and could be regenerated efficiently (>99%).*

Key words: Superparamagnetic nano iron oxide, hydrogel, adsorption, adsorption isotherms.

Introduction

Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders[1]. Therefore, the removal of hazardous heavy metal cations from wastewater has received much attention in recent years. Industrial wastewater particularly in electroplating metal finishing industry, chemical manufacturing and battery manufacturing industries is an important pathway for entry of heavy metals in the environment.

Lead is an industrial pollutant, which enters the ecosystem through soil, water and air[2]. High intake of lead (over 0.05 mg/L, according to the WHO) affects the nervous system because it is highly toxic in nature and Inorganic Lead is an enzyme inhibitor[3]. Best water management system based on scientific methods and effective control of industrial waste and preventing the water resources from toxic metal pollution is an important aspect.

Many methods have been developed to remove heavy metals from wastewater, namely adsorption, chemical oxidation / reduction, precipitation, ion exchange, electrochemical process, membrane filtration and reverse osmosis. Among these methods, adsorption is quite promising due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness[4]. The selection of an effective and economic adsorbent for removal of toxic metal ions requires consideration of both conventional and non conventional materials such as sawdust[5], pomegranate peel[6], rice husk[7], maize cobs[7], papaya seed[8], activated carbon prepared from cashew nut shells[9], dried sunflower leaves[10] and potato peel[11]. Some natural polymers like sodium alginate, chitin, chitosan, pectin, gelatin, carboxy methyl cellulose and their cross- linked microspheres have also shown the good adsorption capacity of heavy metal ions from aqueous solutions[12-20]. In the present decade, several researchers are engaged in synthesizing suitable hydrogels having selective metal ion binding capacity.

The present study aimed to investigate the efficiency of superparamagnetic nano particles of iron oxide loaded poly (acrylamide-co-acrylic acid) hydrogel (superparamagnetic PAA hydrogel) as adsorbent for the adsorption of lead ions from aqueous solution. Superparamagnetic iron oxide nano particles [mostly magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3)] with tailored surface chemistry have been widely used experimentally for numerous applications. All applications require that these nanoparticles should have high magnetization values and sizes smaller than 100 nm with overall narrow particle size distribution, so that the particles have uniform physical and chemical properties[21]. Because of large surface area to volume ratio, the magnetic nanoparticles tend to adsorb toxic metal ions. Nano particles of iron-oxide with high surface energy and surface area have strong adsorption capability, high magnetic properties and involve easy and rapid separation of adsorbent from solution with respect to many inorganic ions and organic matters. The combined technique of sorption and magnetic separation holds the advantageous flexibility, ecofriendly characteristic and recovery of heavy metals is very important and inspiring. The Langmuir, Freundlich and Temkin isotherms were applied to evaluate the adsorption properties in the batch experiments.

Material and Methods

Material: The monomer acrylamide, N, N’-methylene bis acrylamide (cross-linker), potassium per sulphate (initiator), sodium hydroxide pellets, anhydrous ferric chloride and ferrous chloride tetra hydrate were purchased from Molychem, Mumbai, India. Acrylic acid was purchased from Himedia, Mumbai, India. Triple distilled water was used throughout the experiments.

Synthesis of Superparamagnetic PAA Hydrogel: To a mixture of acrylamide and acrylic acid in 1:1 ratio the cross linker (N,N'-methylene-bis-acrylamide) and initiator (potassium per sulphate) were added and heated at 70°C in an electric oven for 1 h. The copolymeric hydrogel so formed was washed with distilled water and cutted into small uniform size pieces. For in-situ magnetization, these pieces were equilibrated in an aqueous solution of ferrous chloride and ferric chloride for 24 h. The nano iron oxide loaded pieces of copolymer were then added into ammonia solution and kept overnight. The magnetic hydrogel was then washed thoroughly with distilled water, dried and crushed into a fine powder, shown in figure 1.

Figure-1
Photograph showing dry superparamagnetic PAA hydrogel

Preparation of Stock Solution: The synthetic solutions were prepared by diluting Pb (II) standard solution (concentration 1000 mg dm^{-3}) obtained by dissolving 0.160g of Pb $(NO_3)_2$ in 100ml distilled water. Fresh dilutions were used in each experiment.

Analytical Technique: The concentration of Pb (II) ions was determined using Atomic Absorption Spectrometer (Varian AA-24-OFS) and each experiment was carried out in triplicate under identical conditions to get the mean values.

Adsorption Experiment: The adsorption experiments were carried out by batch method by varying pH, contact time, adsorbent dose, adsorbate concentration and temperature. For adsorption experiments the superparamagnetic PAA hydrogel (0.1 g) and 25 ml $Pb(NO_3)_2$ solution of 10 mg dm^{-3} concentration at constant pH (4 to 5) and room temperature (27°C) was stirred for 90 minutes which was found to be sufficient time to attain equilibrium sorption. The amount of lead ions present in solution (before and after adsorption) was determined by Atomic Absorption Spectrometer. The sorption degree (percentage removal) and sorption capacity of the sorbent was calculated by the following equations:

$$\text{Sorption degree} = - \frac{(C_o - C_e)}{C_o} \text{ X } 100\ \% \qquad [1]$$

$$\text{Sorption capacity} = \frac{(C_o - C_e)\ \text{X}\ V_{sol}}{m_{sorb}} \qquad [2]$$

Where C_o and C_e (mg dm^{-3}) are initial and equilibrium concentrations of Pb^{2+} ions solutions respectively, V_{sol} (L) is the volume of the lead solution subjected to sorption and m_{sorb} (g) is the weight of sorbent.

Desorption Study: The desorption studies indicate the nature of adsorption and recovery of valuable metals from wastewater and the sorbent. In order to desorb Pb (II) ions from the magnetic adsorbent the polymer was collected, washed and then treated with nitric acid of various strengths ranging from 0.02 to 0.2 M. Desorption efficiency was calculated by using following equation:

$$\text{Desorption efficiency} = \frac{\text{amount of Pb (II) desorbed}}{\text{amount of Pb (II) sorbed}} \text{ X } 100 \qquad [3]$$

Characterization of magnetic copolymer: The adsorbent – "Superparamagnetic PAA Hydrogel" was characterized by XRD, FTIR and TEM analysis.

XRD Analysis: The crystalline nature of the magnetic nanoparticles loaded PAA hydrogel was studied on a Bruker D8 advanced X-ray Diffractometer with scanning range of 20°-80° (2θ) using Cu Kα radiation with wavelength of 1.5406Å (UGC-DAE, Indore, INDIA).

FTIR Analysis: FTIR spectra of adsorbent were recorded using Varian Vertex FTIR Spectrometer (UGC-DAE, Indore, INDIA).

TEM Analysis: The average particle size, size distribution and morphology of iron oxide nanoparticles were examined using a TECNAI – G20 TEM at a voltage of 200 kV. The solvent dispersion of the particles was drop – cast onto a carbon coated copper grid and the grid was air dried at ambient conditions (25 ± 1^{0}C) before loading into the microscope (AIIMS, New Delhi, INDIA).

Results and Discussion

XRD Analysis: The XRD pattern of superparamagnetic PAA hydrogel showed five characteristic peaks (2θ = 30.09, 35.44, 43.07, 56.96 and 62.55), marked by their indices [(511), (311), (400), (511) and (440)]. The position and relative intensities of all diffraction peaks in figure 2 match well with those from the JCPDS file No. 89-5984 for magnetite (Fe_3O_4) and reveal that the prominent phase formed is Fe_3O_4 with resultant nanoparticles of pure magnetic with cubic structure. Magnetite particles are obtained according to the reaction-

$2FeCl_3 + FeCl_2 + 8NH_4OH \rightarrow Fe_3O_4 + 8NH_4Cl + 4H_2O$

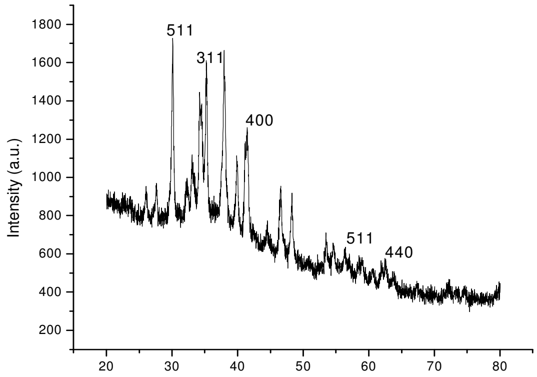

Figure-2
XRD pattern of superparamagnetic PAA hydrogel

FTIR Analysis: Fourier Transform Infrared Spectroscopy (FTIR) of superparamagnetic PAA hydrogel as shown in figure 3, indicated the band at 2930.55 cm^{-1}, assigned to C-H bond of methylene group. The FTIR analysis indicated the band due to acrylamide at 3400 cm^{-1}, 1646 cm^{-1}, 1549 cm^{-1} and 1411 cm^{-1} attributed to N-H stretching, C=O stretching, N-H bending and C-N stretching respectively, which are the characteristics of the amide (CONH$_2$) group. Absorption peaks due to acrylic acid were observed at 1725 cm^{-1} and 1449 cm^{-1} due to C=O and C-O stretching of the carboxylic (-COOH) group and at 3446.24 cm^{-1} due to –OH stretching of –COOH group. The characteristic peak at 566.69 cm^{-1} relates to Fe-O group, which indicates the loading of nano iron oxide particles on PAA hydrogel because the surface of iron-oxide with negative charges has an affinity towards PAA hydrogel, the magnetite nano particles could be loaded into protonated copolymer by the electrostatic interaction and chemical reaction through N,N'-methylene -bis-acrylamide cross linking.

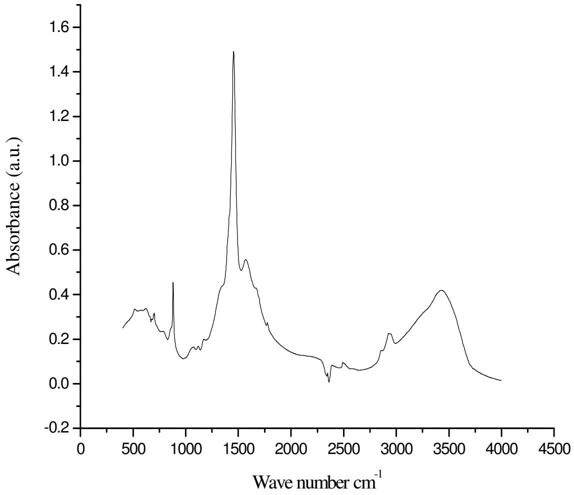

Figure-3
FTIR pattern of superparamagnetic PAA hydrogel

TEM Analysis: The shape, size and morphology of iron oxide nanoparticles were determined through TEM imaging. The TEM images of nanoparticles show almost cubic iron oxide particles with an average size of less than 10 nm as shown in figure 4. Size of these nanoparticles lie within the range 1-9 nm. It should be noted, however, that the majority of the particles were scattered, a few of them showing aggregates indicate stabilization of the nanoparticles. The results represented by TEM images concluded that the particle size of individual nanoparticles seem to be 1-10 nm, whereas majority of nanoparticles exhibit smaller sizes i.e. 5 and 8 nm.

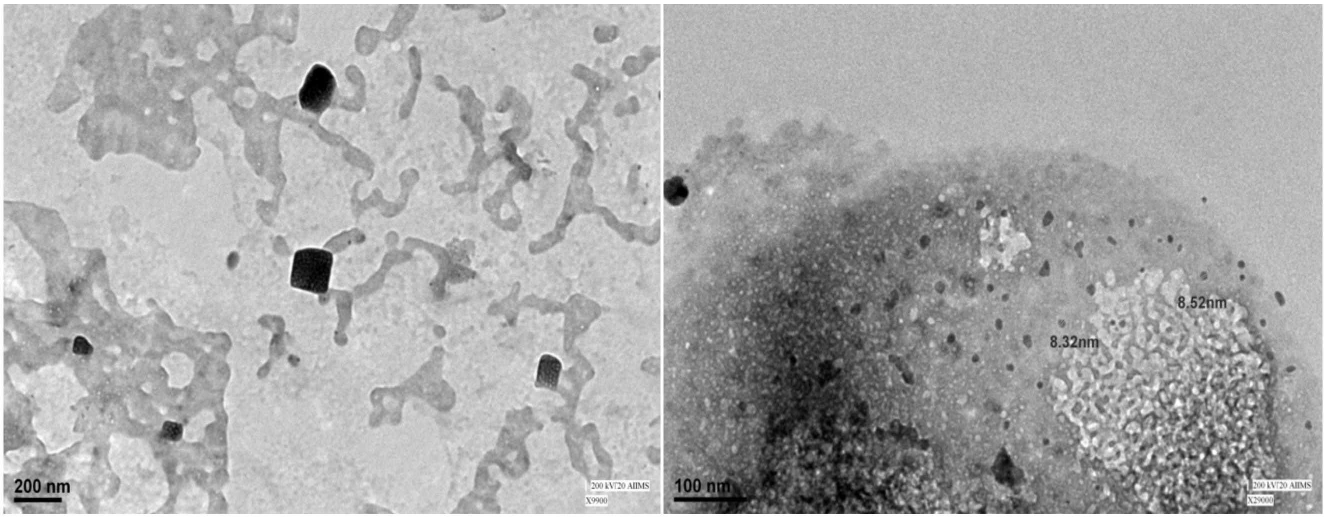

Figure-4
Transmission Electron Micrograph of iron oxide nanoparticles

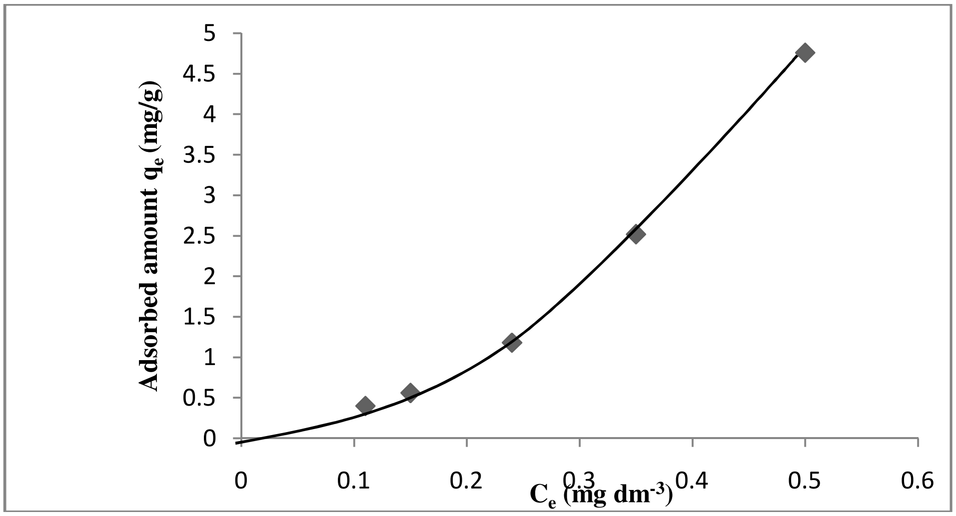

Figure-5
Adsorption isotherm of superparamagnetic PAA hydrogel for Pb (II) ions

Table-1
Constants of Langmuir, Freundlich and Temkin isotherm models for Pb (II) ions

Langmuir constant			Freundlich constant			Temkin constant		
Q_o	b	R^2	K_f	n	R^2	a_s	b	R^2
-2.141	-0.692	0.958	6.5615 x 10^{-1}	0.599	0.992	5.855	2.742	0.860

Adsorption Isotherms: The study of the adsorption isotherm is fundamental and plays an important role in the determination of the maximal capacity of adsorption. The experimental data for the uptake of lead (II) ions by adsorbent, over the studied concentration range were processed in accordance with the three of the most widely used adsorption isotherms: Langmuir, Freundlich and Temkin isotherms.

Langmuir Isotherm: Langmuir equation was applied for adsorption equilibrium study which is based on the assumption that maximum adsorption corresponds to monolayer of adsorbate molecules on the adsorbent surface that the energy of adsorption is constant and that there is no transmigration of adsorbate in the plane of the surface. The isotherm follows the typical Langmuir pattern as shown in figure 5.The linearlized Langmuir isotherm is given by equation 4.

$C_e / q_e = 1 / Q_{o\,.}\, b + C_e / Q_o$ [4]

Where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of solute (mg dm^{-3}), Q_o is the monolayer adsorption capacity (mg/g) and b is a constant related to the free energy of adsorption. The values of constant Q_o and b are given in table 1.

Freundlich Isotherm: The Freundlich equation was applied to describe the analytical results on adsorption. The Freundlich equation proposes an empirical model that is based on sorption on heterogeneous surface and has the form:

$\text{Log } q_e = \log K_f + 1 / n \log C_e$ [5]

Where C_e is the equilibrium concentration (mg dm^{-3}) and q_e is the amount adsorbed per unit mass of adsorbent (mg/g). By plotting log q_e against log C_e, a straight line was obtained with a slope of 1/n and log K_f is the intercept of log q_e. The values of K_f and n are given in table 1.

Temkin Isotherm: The Temkin isotherm model is given by the following equation:

$X = a_s + b \ln C$ [6]

Where C is the concentration of adsorbate at equilibrium (mg dm^{-3}), X is the amount of metal adsorbed per unit weight of adsorbent (mg/g), a_s and b is constants related to adsorption capacity and intensity of adsorption, given in table 1. The correlation coefficient (0.860), showed that adsorption of lead also followed Temkin model. This suggests that lead adsorption may be chemical sorption or chemisorption.

Factors Affecting Adsorption: Effect of pH: The pH of the solution has a significant impact on the uptake of heavy metals, since it determines the surface charge of the adsorbent, the degree of ionization and speciation of the adsorbate. In order to establish the effect of pH on the sorption of lead (II) ions, the batch equilibrium studies at different pH values were carried out in the range of 3 to 8, using 0.1 M HNO_3 and 0.1 M NaOH. It was found that the highest uptake of lead (II) ions was obtained between pH 4 to 5 and at higher pH levels, the adsorption was found to decrease, as shown in figure 6. At higher pH values, the lead ions precipitated as hydroxide which decreased the rate of adsorption, subsequently the percent removal of metal ions [22]. Less sorption at lower pH may be due to the competition of hydrogen ions with metal ions at sorption sites. This means that at higher H^+ ion concentration, the adsorbent surface becomes more positively charged, thus reducing the attraction between adsorbent and the metal ions. In contrast, as the pH increases, more negatively charged surface becomes available, thus facilitating greater metal ion uptake.

Effect of Contact Time: In order to study the effect of contact time on Pb (II) sorption, the experiments were conducted for various time intervals (10 – 120 min) at 10 mg dm^{-3} Pb ion concentration and pH 5, which showed that the sorption of lead (II) ions increases with increasing contact time and attains equilibrium after 90 minutes, shown in figure 7. The plot of percent removal of lead ions Vs time shows that optimum time for maximum uptake (98.87%) was 90 minutes.

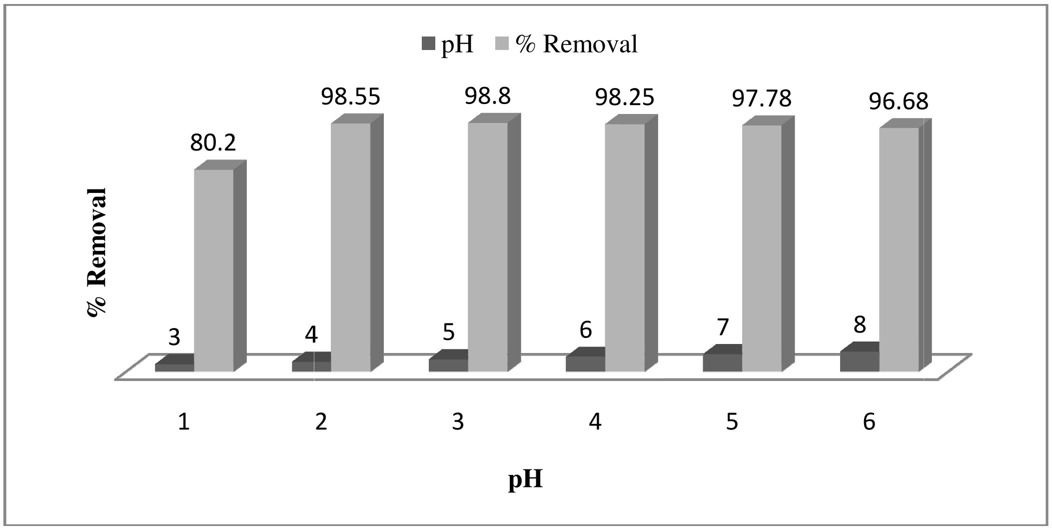

Figure-6
Effect of pH variation on the Pb (II) ions removal through superparamagnetic PAA hydrogel = 0.05 g, time = 90 minutes, temp. = 28 ± 0.2^0C

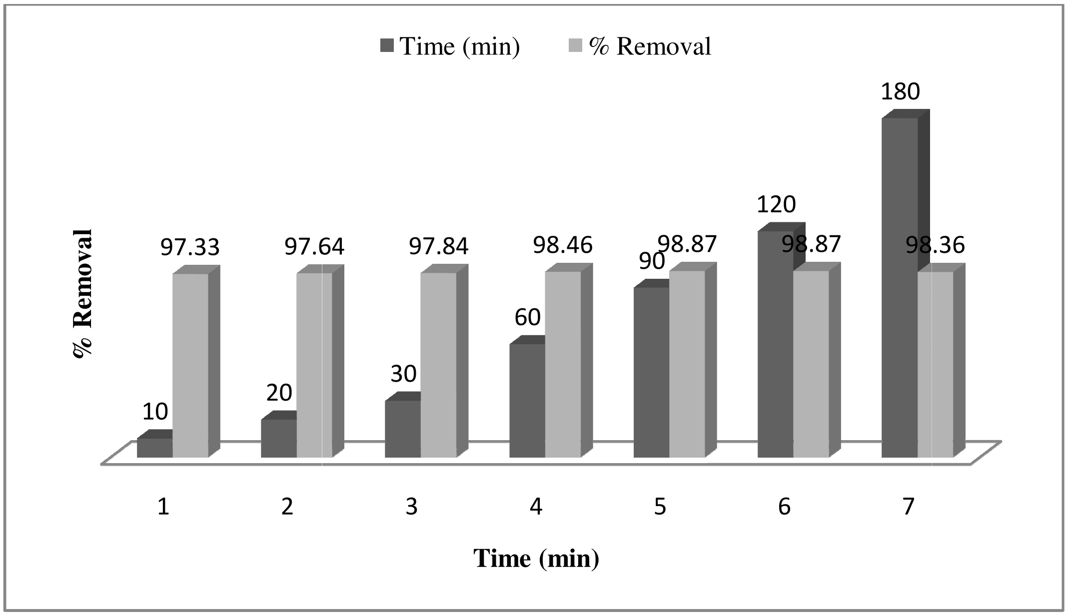

Figure-7
Effect of time variation on Pb (II) ions removal through superparamagnetic PAA hydrogel = 0.05 g, pH = 5, temp. = 28 ± 0.2^0C

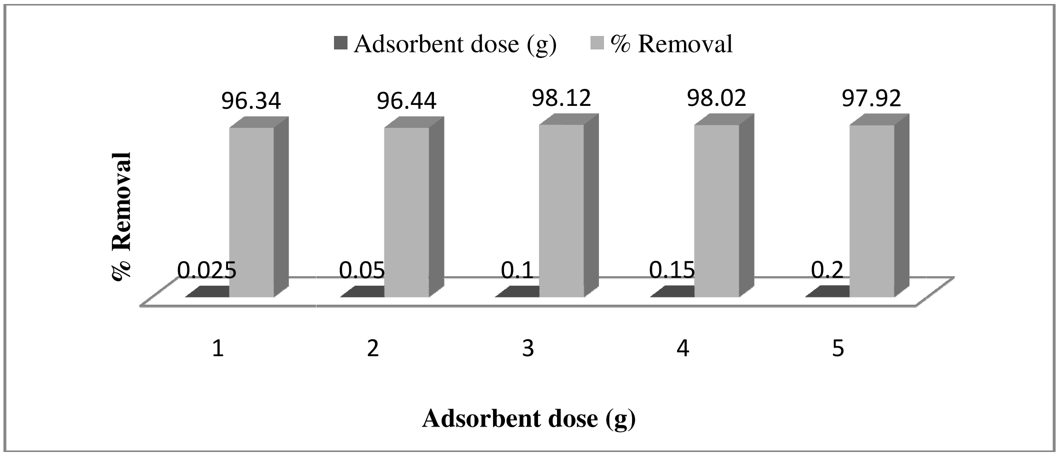

Figure-8
Effect of adsorbent dose variation on Pb (II) ions removal through superparamagnetic PAA hydrogel pH = 5, time = 90 minutes, temp. = 28 ± 0.2^0C

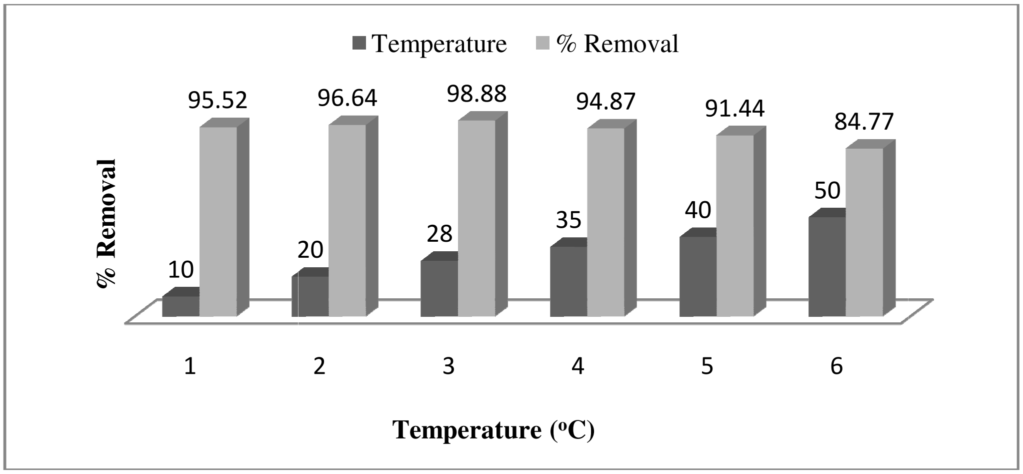

Figure-9
Effect of temperature variation on Pb (II) ions removal through superparamagnetic PAA hydrogel = 0.05 g, pH = 5, time = 90 minutes

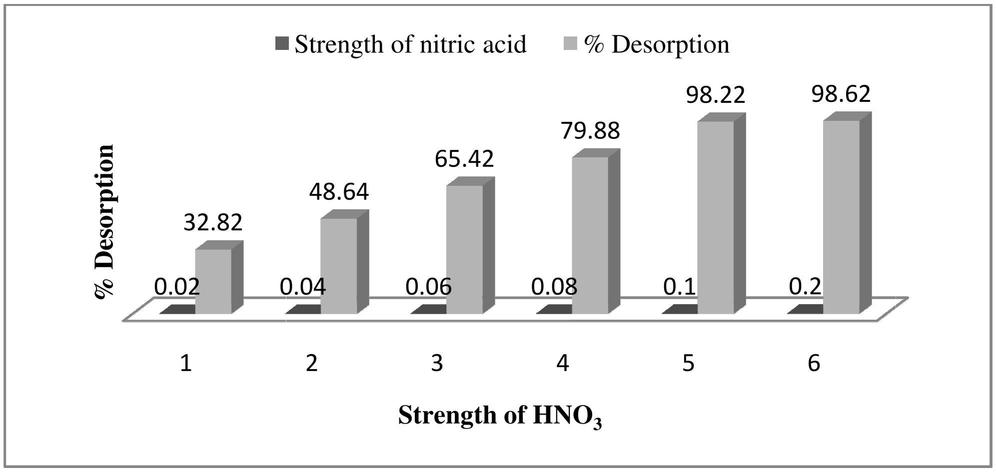

Figure-10
Desorption studies of Pb (II) ions using varies strength of HNO_3 with superparamagnetic PAA hydrogel

Effect of Adsorbent Dosage: The dependence of Pb (II) sorption on adsorbent dose was studied by varying the amount of adsorbent dose from 0.01 to 0.2 g with fixed volume of adsorbate (25 ml) keeping other parameters like pH, contact time and temperature constant. It was observed that maximum removal of Pb (II) ions was obtained with 0.1 g adsorbent as shown in figure 8. This suggests that after a certain dose of adsorbent, the maximum adsorption sets in and hence the amount of ions gets bound to the adsorbent and the amount of free ions remain constant even with further addition of the dose of adsorbent.

Effect of Temperature: Temperature plays an important role on the retention of metal ions by adsorbent. Effect of temperature on removal of Pb (II) ions was studied by conducting adsorption experiment at different temperatures in the range from 10 to 50^o C and it was observed that the adsorption of lead ions increases from 10 to 28^oC, while beyond 28^oC, it decreases as shown in figure 9, which may be explained by the fact that by the increase in temperature, a greater number of active sites may be generated on the adsorbent surface due to the enhanced rate of protonation and deprotonation of functional groups present on the adsorbent surface thus increasing the adsorption of lead (II) ions. At much higher temperatures the observed decrease in adsorption may be due to the weakening of binding forces between lead (II) ions and active sites on the copolymer.

Effect of Initial Concentration: The adsorbate and adsorbent interaction was studied by performing the adsorption experiments with different lead ion concentrations in the range of 1.25 to 20 mg dm^{-3} and it was observed that with the increase in initial Pb (II) ion concentration, the percent removal of metal ions also increased. The observed increase is quite obvious, as on increasing the concentration of solute, greater number of metal ions arrives at interface and thus get adsorbed.

Desorption Studies: Desorption results indicated that the complete desorption of Pb (II) ions took place by 0.1 M HNO_3 as shown in figure 10.The polymer showed almost the same metal ion adsorption capacity after repeated regeneration. It may be stated that in the acid medium protons compete with lead ions and displace the maximum amount of adsorbed lead. Hence, ion exchange mechanism is important in connection with adsorption-desorption process for adsorbent.

Conclusion

The superparamagnetic nano iron oxide loaded poly (acrylamide-co-acrylic acid) hydrogel has been found to be very effective adsorbent for the removal of Pb (II) ions from aqueous solution. The maximum removal of metal ions occurred between the pH ranges 4 to 5 at 28^0C within 90 minutes. The superparamagnetic PAA hydrogel could be repeatedly used in the adsorption studies by adsorption – desorption cycle without detectable losses in their initial adsorption capacities. The maximum removal of Pb (II) ions from aqueous solution was observed to be 98.87%, which proves this adsorbent to be superior among other adsorbents.

Acknowledgement

The authors would like to express thanks to the Department of Atomic Energy, BRNS, BARC, Mumbai, India for providing financial assistance. Authors are also grateful to UGC-DAE Consortium for Scientific Research, Indore and AIIMS, New Delhi, India for various instrumental analysis.

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