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New Nano-Adsorbents for the Removal of Chromium (III) and Mercury (II) from Aqueous Solutions

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Abstract

Polyvinyl alcohol/ glycerin- magnetic iron oxide nanoparticles (PVAGLPs) have been synthesized successfully by hydrothermal method. The as-prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectra (FTIR). The adsorbed activities of the polyvinyl alcohol/ glycerin- magnetic iron oxide nano particles (PVAGLPs) were carried out varying parameters for adsorption Cr (III) and Hg (II) ions. Adsorption experiments were carried out varying parameters such as initial metal ion concentration (10-100 ml/g), pH (1-9), contact time (10-120 min) and weight of adsorbents (0.1-0.6 g). The increase in metal uptake with increase in dose of adsorbent from 0.1 – 0.6g was due to the increase in surface area and number of active sites for the adsorption. Shows that the adsorbent of metal ions increased from 65 to 92% and 54 to 82% for Hg (II) and Cr (III) respectively. Optimum conditions for the removal of Cr (III) and Hg (II) with PVAGLPs are: 0.4 g of adsorbent, concentration 50 ppm, at 25°C and at pH 5.0 for Cr (III) and 4.0 for Hg (II).

Key words: *New Adsorbent, Environmental Pollution, Magnetic Nanoparticle, PVAGLPs.*

Introduction

The toxic heavy metals present in wastewater, effluents and soils are becoming a major environmental concern and multi-metal pollution is the usual situation in environmental media [1]. Heavy metals are dangerous because they tend to bio accumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment [2]. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted [3]. Heavy metals

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can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and ground water [4, 5].

There are several methods to treat the metal contaminated effluent such ion exchange, electrolysis, separation by membrane, adsorption, etc., but the selection of the wastewater treatment methods is based on the concentration of waste and the cost of treatment [6-8]. Heavy metal ions, aromatic compounds (including phenolic derivatives, and polycyclic aromatic compounds) and dyes are often found in the environment as a result of their wide industrial uses [9-11]. A waste containing soluble toxic heavy metals requires concentration of the metals into a smaller volume followed by recovery and secure disposal. Heavy metals can be removed by adsorption on solid matrices [12-14]. Much attention has recently been focused on biopolymers as bio-adsorbents. They are naturally produced by all living organisms. [15-17].

In this study, a novel sorbent material prepared by coating Fe_3O_4 magnetic nano particles with polyvinyl alcohol/ glycerin was developed for the removal of heavy metal ions from water.

The as-prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectra (FTIR). The adsorbed activities of the polyvinyl alcohol/ glycerin-magnetic iron oxide nano particles (PVAGLPs) were carried out varying parameters for adsorption Cr (III) and Hg (II) ions.

Experimental

Materials

Polyvinyl alcohol (PVA) (Mn= 72,000) and glycerol (Mn= 92/10, 78 % purity) purchased from Merck company. All other chemicals were used as received without further purification. Standard solution of Cr(III) was prepared by dissolving 7.6960 g $Cr(NO_3)_3 \cdot 9H_2O$ (reagent grade from Merck, Darmstadt, Germany) in 250 ml deionized water and diluting to 1 L adding HNO_3 to obtain a final concentration of 2% (v/v); this was checked against a titrisol standard solution from Merck (Darmstadt, Germany). The Hg (II) stock solution was prepared by dissolving 1 g of 5 M nitric acid prior to dilution with deionised water to 1 L volume. Standard solutions of the desired concentrations (10–100 μgmL^{-1}) were prepared by successive dilutions of the corresponding stock solutions.PH adjustments were made with digital pH-meter (Sartorius, Model PP-20) using HCl (0.1 mol L^{-1}) and NaOH (0.1 mol L^{-1}). Stock solution (1,000 mg L) of Hg(II) was prepared by dissolution of appropriate amounts of mercury (II) nitrate (Redial, Hannover, Germany) and stored it in the dark at 4°C. A stock solution of Cr (III) (520 mg/L) was prepared by dissolving analytical reagent grade chromium nitrate (Cr $(NO_3)_3 \cdot 9H_2O$) (Sigma) in distilled water. All working solutions were prepared by adequate dilution of the stock solution with distilled water.

Synthesis of Fe_3O_4 MNPs

Fe_3O_4 MNPs were synthesized by a reported chemical co-precipitation technique of ferric and ferrous ions in alkali solution with minor modifications [16]. $FeCl_2 \cdot 4H_2O$ (1.99 g) and $FeCl_3 \cdot 6H_2O$ (3.25 g) were dissolved in deionized water (30 mL) under Argon atmosphere at room temperature. A NH_4OH solution (0.6 M, 200 mL) was then added drop wise (drop rate = 1 mL min1) to the stirring mixture at room temperature to reach the reaction pH to 11. The resulting black dispersion was continuously stirred for 1 h at room temperature, and heated to reflux for 1 h to yield a brown dispersion. The magnetic nano particles were subsequently separated by a magnetic bar and washed with deionized water until it was neutralized.

Synthesis of PVA-GLNPs

In a typical synthetic process, PVA (5g) were well-dispersed in deionized water (100 mL) under magnetic stirring at 60 °C for 5 h time. Then 100 ml of Fe_3O_4 in water for 15 minutes using an ultrasonic bath was suspended. At this stage, soluble PVA, sulfuric acid and a certain amount of cross-linking Glyceraldehyde to 50% PVA, Fe_3O_4 nano particles were added to the suspension. The mixture was stirred using a magnetic stirrer. After 20 minutes, PVA-GLNPs nano particles were formed, and the particles using a magnetic field strength of the solution was separated. These particles are then washed with sodium hydroxide ions and water and finally dried in an oven for 24 hours, respectively.

Adsorption Experiments

The adsorption studies were carried out at 25 ± 1°C. pH of the solution was adjusted with 0.1 N HCl. A known amount of adsorbent was added to sample and allowed sufficient time for adsorption equilibrium. Then the mixture was filtered and the remaining ions concentration was determined in the filtrate using flame atomic absorption spectrophotometer (SHIMADZU, AA-680). The effect of various parameters on the rate of adsorption process was observed by contact time, initial concentration, initial pH of solution, and temperature. The solution volume (V) was kept constant 50 mL. The adsorption (%) at any instant of time was determined by the following equation:

$$\text{Dye adsorption (\%)} = (C_o - C_e) \times 100 / C_o \quad (1)$$

Where Co is the initial concentration and Ce is the concentration of the metal ions at equilibrium. To increase the accuracy of the data, each experiment was repeated three times and average values were used to draw the graphs.

Results and discussion

SEM was used to examine the surface morphology of Fe_3O_4 nano particle (figure 1a). TEM micrographs were TEM micrographs were also used to examine the shape and particle sizes of the Fe_3O_4 nano particle (figure 1b).The image showed that Fe_3O_4 nano particle had mean diameters of about 50 nm. Surface characteristics of the samples SEM provides information on the structures, as shown in figure 2. Very uniform particles with a favorable morphology could be observed for the PVA-GLNPs, as seen from the high magnification image in figure 2, which suggests that a core material of pure Fe_3O_4 was uniformly enclosed or overlapped with PVA-GL via the hydrothermal reaction.

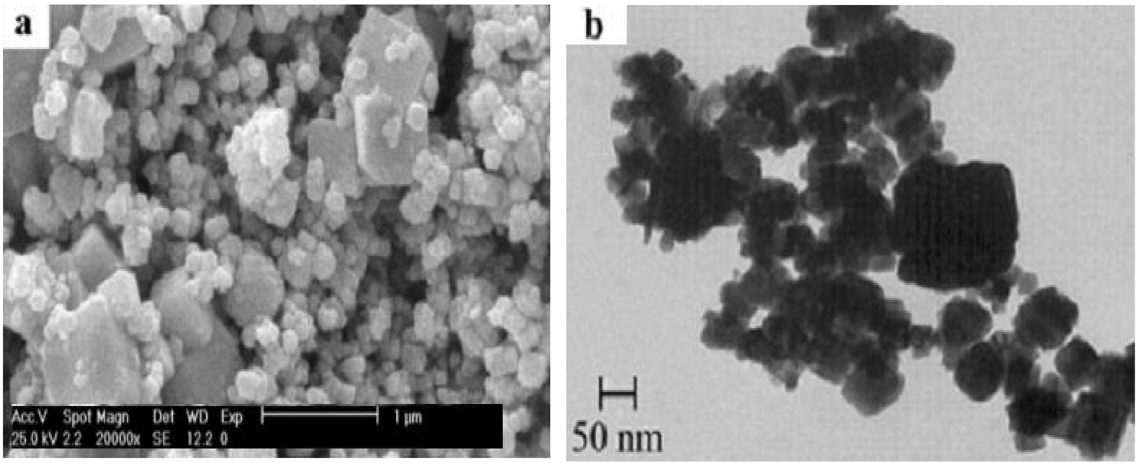

Figure 1. SEM micrograph of Fe_3O_4 nano particle (a) and TEM image of Fe_3O_4 nano particle (b).

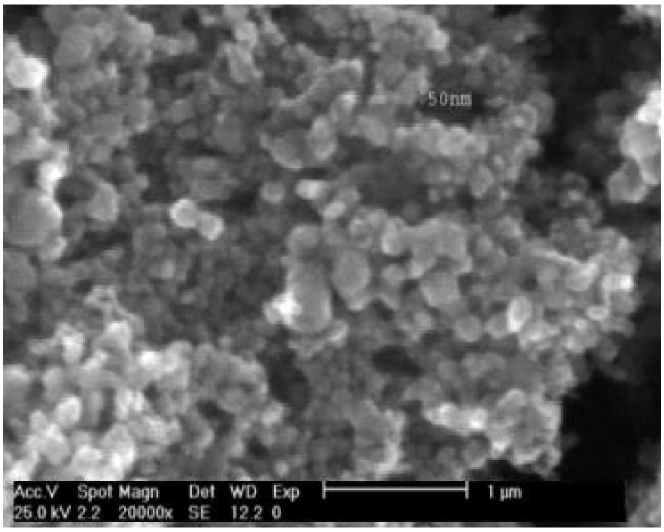

Figure 2. SEM micrographs of PVA-GLNPs.

The Fourier Transform Infrared (FTIR) spectrum of synthesized PVA-GLNPs is shown in figure 3. The presence of some functional groups on the surface of the particles is obvious. The most significant peaks appeared at 1310 cm^{-1} and 1615 cm^{-1} and are related to the stretching mode of the carboxylic group [7]. There are other peaks at 1030 cm^{-1} and 1250 cm^{-1} that are related to C-O and C=O respectively in the carboxylic group. Finally, the broad stretched peak at 3445-1645 cm^{-1} represents OH.

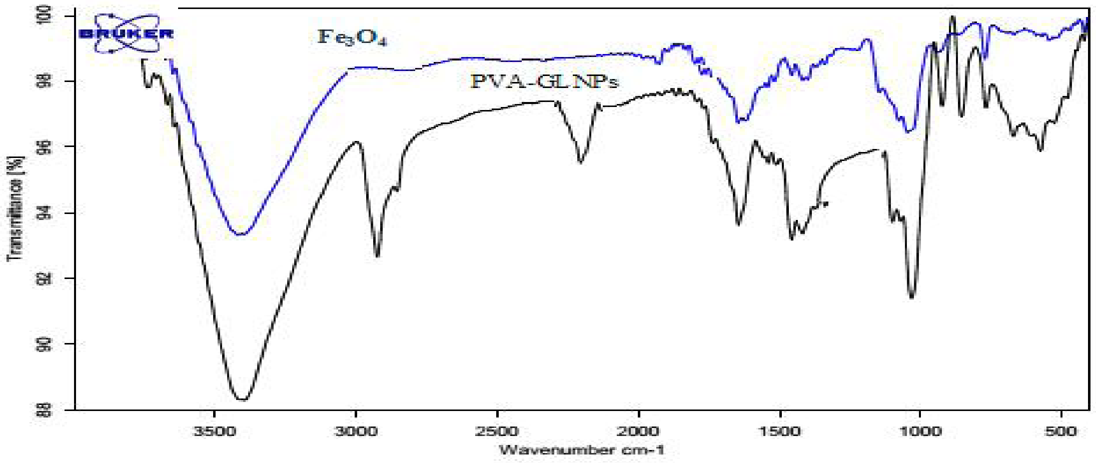

Figure 3. FT-IR spectra of PVA-GLNPs.

The X-ray diffraction (XRD) pattern of synthesized PVA-GLNPs (figure 4) indicates that magnetite particles have a highly crystalline cubic spinal structure. The diffraction peaks at 31, 35.7, 43.2, 53.3, 57.5, 63.1 and 66.4° responded to cubic Fe_3O_4 lattice, respectively. The cubic spinal structure of Fe_3O_4 is proven by comparing the XRD pattern with others reported in literature [9, 12].

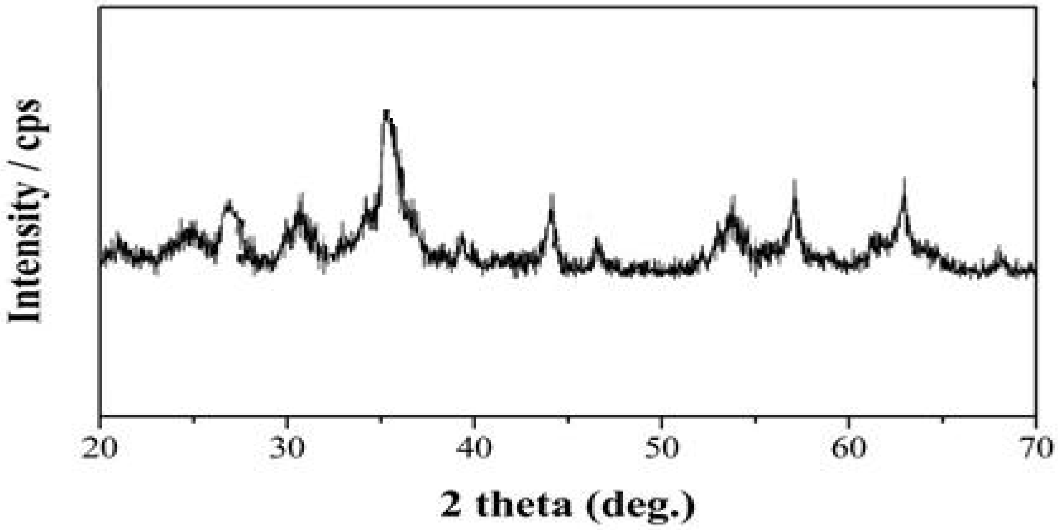

Figure 4. XRD of PVA-GLNPs.

Metal sorption is critically linked with pH and the effect of pH of a solution is an important controlling factor in the sorption experiment. The pH value played a very important role in the use of nano-adsorbents as supports in the metal ion adsorption process. The number of adsorption sites available for heavy metal ions decreased as the number of protonated metal-binding absorbent groups increased. The pH in solution has been identified as the most variable governing metal adsorption on sorbent. This is partly due to the fact that hydrogen ions themselves are strongly competing adsorbents. The pH solution influences the specification of metal ions and the ionization of surface functional groups [18-21]. The effects of pH for Hg (II) and Cr (III) removal are shown in figure 5. The maximum removal was 91% for Hg (II) and 82% for Cr (III). These experimental results indicate that the binding of Hg (II) is more pH dependent than those of Cr (III). High adsorption at higher pH values implies that metal ions interact with PVA-GLNPs by chelating.

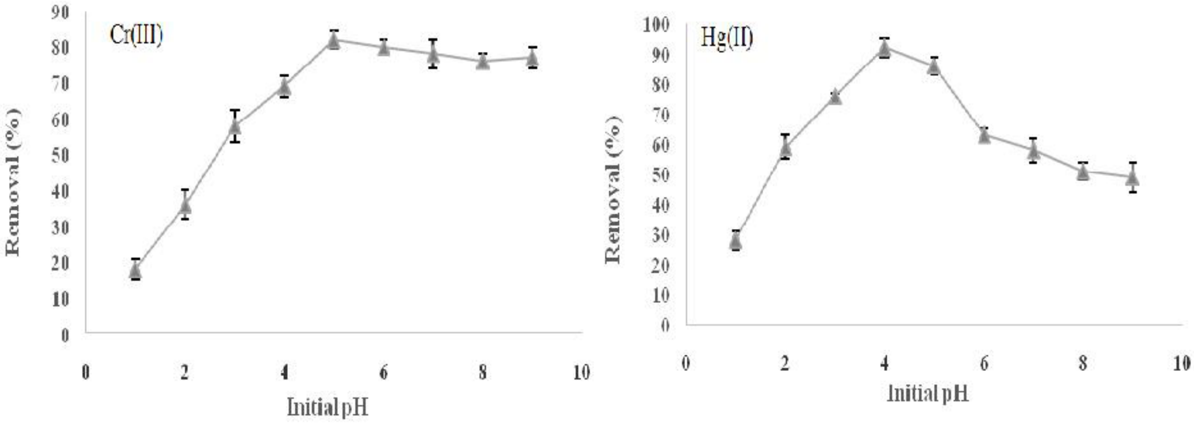

Figure 5. Effect of pH.

The effect of adsorbent dosage is shown in figure 6. Removal increased with the increase in the sorbent mass. Figure 6 shows that the amount of Hg (II) and Cr (III) ion removed as dosing mass was increased. An increase in the absorbent dosage from 0.1 to 0.6 g/L led to an increase in the removal efficiency of Hg (II) from 61.0 to 93.3 and Cr (III) from 52.6 to 82.0.

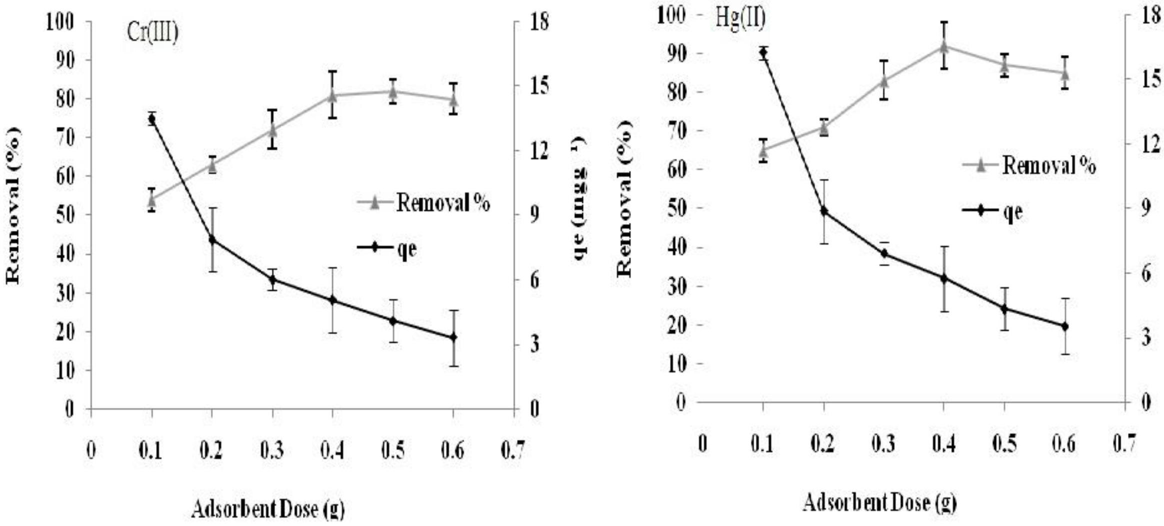

Figure 6. Effect of Adsorbent Dose.

Influence of contact time on adsorption of Hg (II) and Cr (III) on PVA-GLNPs was investigated in the range of 10–120 min for the initial concentration of 50 ppm for each metal ion (figure 7).

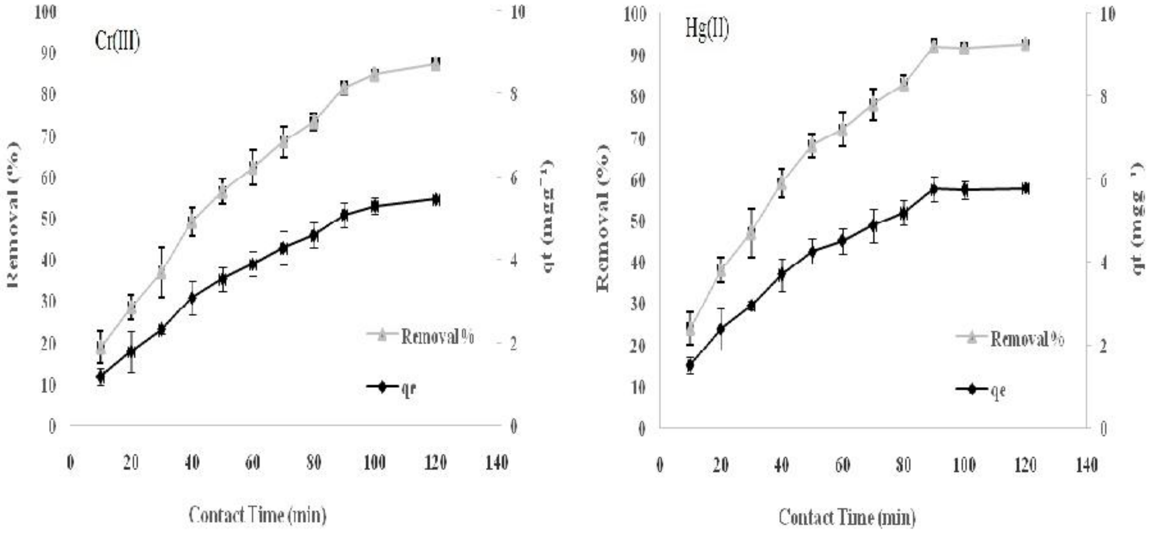

Figure 7. Effect of Contact Time (min).

Maximum rate of removal occurred within 60 min of contact time there after removal rate became slow and after 60 min of contact time no change was observed for Hg (II) (72%) and Cr (III) (62%). Influence of initial concentration was one of the effective factors on adsorption efficiency. The percentage of Hg (II) and Cr (III) adsorption on PVA-GLNPs was studied as a function initial concentration of in the range of 10-100 ppm. The results obtained are present in figure 8.

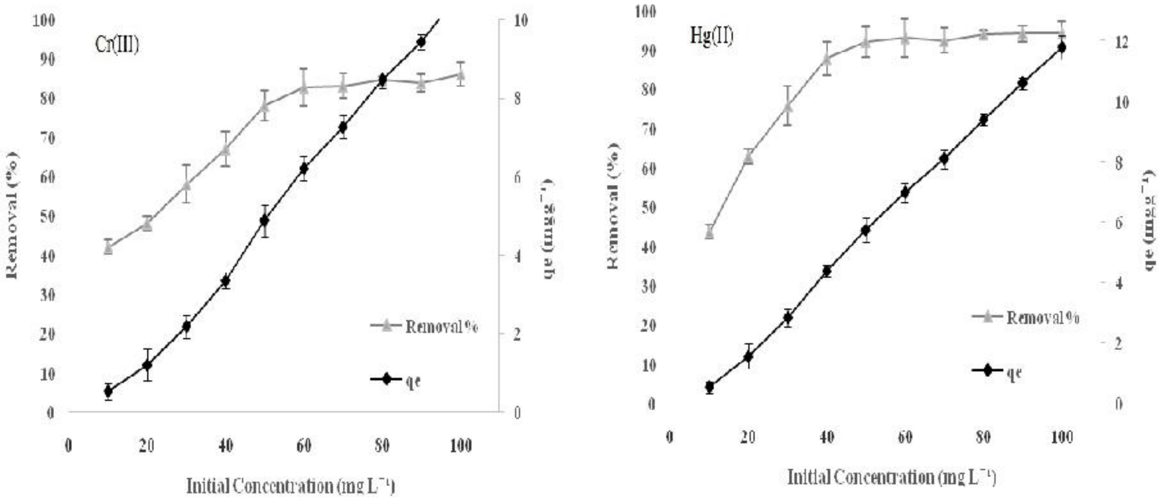

Figure 8. Effect of Initial Concentration.

The percentage adsorption increases with increase in initial concentration of the Hg (II) and Cr (III) for PVA-GLNPs. It was observed that adsorption yield increased with increase in initial concentration of the dye. Minimum adsorption was 42% for 10ppm concentration to maximum adsorption value 86% for 100 ppm concentration of Cr (III) and minimum adsorption was 43.7% for 10ppm concentration to maximum adsorption value 94.2% for 100 ppm concentration of Hg (II). This may be due to available active sites and increase in the driving force of the concentration gradient, as an increase in the high initial concentration of the ions.

Conclusion

The results of this study showed that alcohol/glycerin-magnetic iron oxide nano particles (PVAGLPs), could be employed as a sorbent for the removal of chromium (III) and mercury (II) from aqueous waste solutions. Optimum conditions for the removal of Cr (III) and Hg (II) with PVAGLPs are: 0.4 g of adsorbent, concentration 50 ppm, at 25°C.

Acknowledgement

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References

[1] S. Ding, Y. Sun, C. Yang, B. Xu, *Min. Sci. Tec.*, 19, 489 (2009).

[2] D. Mohan, S. Chander, *J. Haz. Mat.*, 137, 1545 (2006).

[3] Z. Abbasi, M. Alikarami, *Biochemistry and Bioinformatics*, 1, 1 (2012).

[4] Z. Abbasi, M. Alikarami, A. Homafar, *Inorg. Chem. An Indian J.,* 8, 69 (2013).

[5] S. R. Chowdhury, E. K. Yanfu, *J. Env. Man.*, 91, 2238 (2010).

[6] P. Businova , J. Chomoucka , J. Prasek, R. Hrdy , J. Drbohlavova, P. Sedlacek, *J. Hubale, Brno, Czech Republic, EU*, 9, 21 (2011).

[7] G. Marcelo, J. M. Martinho, J. P. Farinha, *J. Phys. Chem. B.*, 117, 3416 (2013).

[8] S. Keshavarz, X. Yaolin, S. Hrdy, C. Lemely, *IEEE Transations On Magnetic*, 46 (2010).

[9] S. Parsons. IWA Publishing, London, UK (2004).

[10] J. F. Guo, B. Ma, A. Yin, K. Fan and W. L. Dai. *Applied Catalysis B: Environmental*, 101, 580 (2011).

[11] J. Xia, A. Wang, X. Liu and Z. Su. *Applied Surface Science*, 257, 9724 (2011).

[12] M. M. Curri, R. Comparelli, P. D. Cozzoli, G. Mascolo and A. Agostiano, *Mat. Sci. Eng.* C., 23, 285 (2003).

[13] X. Liu, Q. Hu, X. Zhang, Z. Fang, Q. Wang, *J. Phys. Chem. C.,* 112, 12728 (2008).

[14] S. Lidia, J. Claudia, N.K. Santosh, *Water Research*, 2129 (2001).

[15] A. Li, J. Zhang, A. Wang, *J. Appl. Polym*. Sci., 103, 37 (2007).

[16] Y. K. Sun, M. Ma, Y. Zhang, N. Gu, *Colloids Surf A: Physico-chem. Eng. Aspects*, 245, 15 (2004).

[17] B. D. Kevadiya, G.V. Joshi, H. M. Mody, H. C. Bajaj, *Appl. Clay Sci.,* 52, 364 (2011).

[18] J. L. Hall, *J. Exp. Botany,* 53, 1 (2002).

[19] H. Marschner, Mineral nutrition of higher plants, 2nd ed., London, Academic Press, (1995).

[20] A. Leusch, Z. R. Holan, B. Volesky, *J. Chem. Tech. Biotechnol.*, 62, 279 (1995).

[21] Y. Sag, T. Kutsal, *Biochem. Engin. J.*, 6, 145 (2000).