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Metal Nanoparticles as Effective Adsorbents to Treat Mining Industry Wastewater

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Abstract

Water containing various toxic contaminants is one of the most severe problems throughout the world. Many technologies have been used to treat such water in the past few decades. Current technologies contain the process of ion exchange, electrochemical methods and flotation. The use of nanotechnology is gaining importance every day in this line. Aluminium titanium, silicon and iron oxides are gaining importance as iron oxide is the cheapest metal available in good quantity in nature which also has suitable magnetic a good property when compared to other oxides. Its properties can be exploited to remove heavy toxic metal pollutants from contaminated water. In the present work, nanoparticles of iron oxide were used to remove the Lead (Pb) (II) ions present in the mining industrial wastewater. The efficiency of adsorption was studied by the Freundlich mathematical model. The results show that the magnetite nanomaterial can be used effectively as a potent adsorbent material in Standard Temperature and Pressure (STP).

Keywords: Continuous Adsorption, Heavy Metals, Iron Oxide, Nanoparticles, Wastewater

1.0 Introduction

Due to various human activities, there is a severe threat to land, air and water. Water pollution is affecting the environment every day, which results in scarcity of drinking water in addition to the resources of water. Among the contaminants, the inorganic pollutants were found to be intensely destructive due to their high toxicity and non-biodegradability followed by infectious agents. The presence of metals in water is the primary source of inorganic pollutants. The most popular heavy metals are Lead (Pb), Zinc (Zn), Mercury (Hg), Nickel (Ni), Cadmium (Cd), Copper (Cu), Chromium (Cr) and Arsenic (As) (Naef *et al.,* 2021)[1]. Tin, lead, arsenic and cadmium are introduced to the environment by anthropogenic activities, which slowly diffuse into the surrounding water and soil. Mining industry wastes are the primary source of contamination in the surrounding environment, leading to soil and water pollution, habitat destruction, adverse health effects for nearby communities and the release of harmful substances such as heavy metals, toxins and acid mine drainage, contributing to long-term ecological damage and biodiversity loss (Holopainen, 2003)[2].

"Nanotechnology" is a new area that has vast applications in the field of engineering and is implemented at the nanoscale (P. Kumari and Siddiqui, 2019)[3]. Nanotechnology word refers to the use of nanoparticles of size less than 100 nanometers (Khan *et al.,* 2019)[4]. Various metal nanoparticles are used as adsorbents for the treatment of wastewater. Silver predominates the list, followed by copper and zinc. Due to the availability and price of these metals, they are expensive for domestic purposes only. When compared to silver, copper and zinc, iron nanoparticles have good magnetic properties,

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which can be utilised to remove heavy metals and also to disinfect the infectious particles present in the wastewater (Ping *et al.* 2017)[5]. In the present work, the nano iron particles were considered to remove the lead from the wastewater.

2.0 Motivation

In the present work, an attempt was made to treat mining industry wastewaters. The main focus was to adsorb the heavy metals using adsorbents by applying the basic principles of nanotechnology to solve the problems related to environmental issues, and more concerned with improving the quality and reuse of the water for the agriculture sector. Many researchers used scientific methods like adsorption, evaporation, floatation, oxidation, and bio-sorption techniques for the treatment of water, but some of these methods were not competent for the treatment of wastewater in bulk quantity, and are more competent for lab scale. Among all these techniques, the technique of adsorption was economically favourable and technically easy to separate and operate.

There has been a lot of interest recently in using magnetite technology to address environmental issues. These magnetite particles (Fe_3O_4) can be used to adsorb lead, nickel, cadmium, chromium and arsenate from wastewater. Alkalinity, hardness, and organic compounds may all be eliminated with the help of magnetite particles. Fe_3O_4 nanoparticle synthesis is strongly favoured for prospective applications and basic research. as it is efficient, economical, scalable, biocompatible, biodegradable, and non-toxic. A major area of focus for researchers is the creation of effective green chemistry techniques for the synthesis of metal nanoparticles (Siavash *et al.*, 2011)[6].

3.0 Theory and Concepts

Magnetic iron oxide nanoparticles (NPs) are novel functional materials, widely used in the field of biotechnology. Iron oxide NPs consist of maghemite (γ-Fe_2O_3) and, or magnetite (Fe_3O_4) particles with particle sizes varying from 1 and 100 nanometers. These nanoparticles have applications in magnetic data storage, bio-sensing, drug-delivery catalysis, biosensors, ferrofluids, magnetic separations and MRI contrast agents (Teja *et al.*, 2009)[7]. The nanoparticles have a very high specific surface, which increases the binding capacity and excellent dispensability in solutions. Magnetic nanoparticles with sizes ranging from 2nm to 20nm exhibit super para magnetism which can be magnetised by an external magnetic source. This property gives rise to additional stability for magnetic nanoparticles in solutions (Attarad *et al.* 2016)[8]. Iron oxide nanoparticles in extreme temperatures and high pH will conjugate with other biomolecules, which leads to an increase in adsorption. This opens horizons of opportunities for the development of iron oxide nanoparticle-based applications.

4.0 Materials and Methods

In the present work, nano-magnetite particles from iron oxide were synthesised in the Biotech department of R.V. College of Engineering using the green synthesis method. All the chemicals used were procured from Merck India Pvt Ltd, and for the characterisation of nanoparticles, Fourier-Transform Infrared spectroscopy (FTIR) in-house facilities were used.

5.0 Experimentation

5.1 Preparation of Standard Stock Solution

A Standard stock solution containing 100ppm of lead ions is prepared by dissolving 150.85mg of lead nitrate salt in one litre of distilled water. From the standard stock solution, 20, 40, 60, 80, and 100ppm concentrations of lead solution were prepared by dilution.

5.2 Batch Adsorption of Lead Pb (II)

100ml of known concentration of the prepared stock solution is taken in 6 different conical flasks. The composite nanoparticle is varied from 10mg to 60mg in multiples of 10mg into each of the conical flasks. The contents in the conical flask were thoroughly mixed using an orbital shaker (100rpm) for an hour. After mixing, the nanoparticles were filtered using vacuum filtration at a pressure of 500mm Hg using Whatman filter paper (No 41). The absorbance of the filtrate was measured using an Atomic Absorption Spectrometer at 270nm, and the concentration of residual Pb (II) ions in the filtrate (free of nanoparticles) was determined using a standard graph.

5.3 Adsorption Isotherms

To study the behaviour and effectiveness of adsorption, the Freundlich mathematical equation (Mulu Berhe Desta, 2013)[9] is used. As per the Freundlich equation, the final

concentration of the lead ions (C^*) adsorbed is plotted against the amount of the lead ions present in the solution ($\ln(V(C_0 - C^*)$), where, C^* is the final Concentration of lead ions adsorbed in mg/l, C_o is the initial concentration of lead ions present in the solution in mg/l, V is the ratio of adsorb-ate to adsorbent in m^3/Kg. From Figure 2, the slope value determines the adsorption based on the value 0 to 10.

5.4 Continuous Adsorption of Lead Pb (II)

The continuous adsorption is carried out using the adsorption column of internal diameter of 30 mm and 120mm in diameter. The adsorption column is filled with nanoparticles to a bed height of 10mm.

100ml of the prepared stock solution (100ppm) is fed to the column at a flow rate of 60 ml/hr. The stock solution (fractions) coming out from the adsorption column is collected every 5 minutes for an hour. The concentration of residual Pb (II) ions in the collected fractions is determined by measuring the absorbance at 270 nm by AAS. The graph of time v/s C^*/C_0 was plotted (Fatiha Benmahdi *et al.* 2018)[10] and used for the behaviour of continuous adsorption studies.

5.5 X-Ray Diffraction

To ascertain the crystalline phase and chemical makeup of the produced samples, XRD measurements of the reduced magnetite nanoparticles were performed using XRD equipment operating at a voltage of 40 KV, a current of 30 mA, and Cu K (Kα (1.5406 Å)) radiation. The samples were collected for this purpose in lids and placed in the sample container for examination.

6.0 Results and Discussion

6.1 Effect of Nanoparticles on Lead Pb (II)

The effect of iron nanoparticles on the adsorption of Pb (II) (100ppm) is presented in Figure 1. Initially, there is a good amount of increase in adsorption from 25.4% to 76.91% for the increase in iron nanoparticles from 10mg to 40mg. After this there is a little increase in adsorption from 76.91% to 86.14 for an increase in nanoparticles increase from 40mg to 50mg. For further increase in the nanoparticles, the adsorption increases from 86.14% to 93.07%, which is almost constant; this indicates that the active sites on the surface of nanoparticles were almost exhausted.

6.2 Freundlich Mathematical Model

Figure 2 represents the graphical representation of ln (v (C_0 – C^*)] v/s ln C^*, from Figure 2 the slope and intercept values are 4.71 and 29.32, which represents the adsorption capacity (Slope) and intensity (Intercept). The value of slope indicates the adsorption of lead on the nanoparticles fits the Freundlich adsorption model, which indicates that the iron nanoparticles process good characteristics for adsorbing the lead ions.

6.3 Breakthrough Curve

Continuous adsorption of Pb (II) ions on nanoparticles is carried out in a fixed bed adsorption column of an internal diameter of 30mm and bed height of 10mm. The lead ion solution of concentration 100ppm was continuously sent to the fixed bed column at a rate of 60 ml/hr and the contents coming out from the fixed bed column were analysed for absorbance for a time interval of every 5 minutes. The graphical representation of time v/s C^*/C_0 is presented in Figure 3.

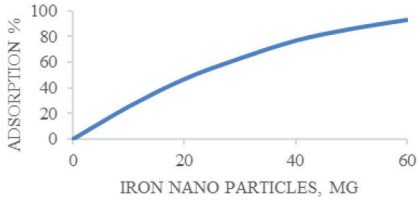


Figure 1. Effect of nano iron particles on Pb.

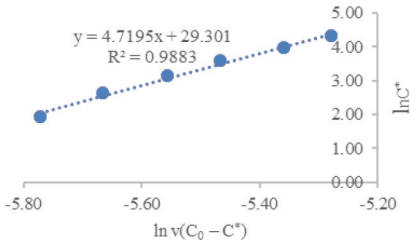


Figure 2. Freundlich isotherm.

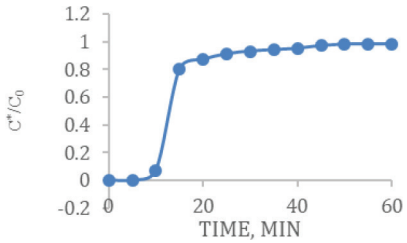


Figure 3. Breakthrough curve.

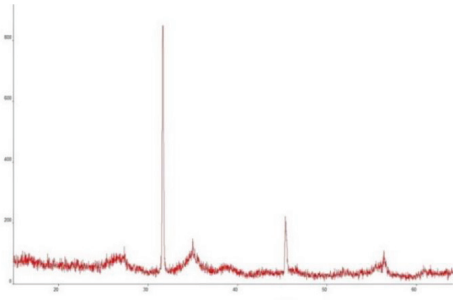


Figure 4. XRD of magnetite nanoparticles.

nanoparticles. From the results of batch adsorption the slope (n) value was found to be 4.719 indicating good adsorption, and also indicating the nanoparticles synthesised can be used as potential adsorbent, to remove heavy metal pollutants from mining industry wastewaters. From the results of continuous fixed bed adsorption, the breakpoint and exhaust point were at 12 minutes and 28 minutes, respectively. Hence magnetite nanoparticles can be used for the treatment of wastewater, which will be cost-effective compared to silver and copper, safe and non-toxic.

Table 1. Parameters as per the Debye-Scherrer equation

S No	Peak 2θ	Wave Length A^0	Cos θ	Width of baseline in degrees	Width of baseline in radians	D nm
1	32.1	1.54	0.847	0.3	0.02	104.16
2	47.2	1.54	0.679	0.5	0.03	77.96
Average particle size(nm)						91

From Figure 3 the breakpoint (T_B) occurred at 12 minutes and the exhaust point (T_E) at 28 min, from these breakpoints and exhaust time the, space time ($T = T_B/T_E$) was found to be 0.42.

6.4 X-Ray Diffraction Analysis

The results of the XRD analysis of nanoparticles are presented in Table 1 and its spectrum is in Figure 4. In Figure 4, the 2theta peaks (X-axis) observed at 32.1° and 47.2° attributed to crystal planes of magnitude (Y-axis) 810 and 180 respectively at, wavelength 1.54 A^0. The position and the relative intensity of the diffraction peaks matched with standard XRD data (Abhijeet Mishra *et al.*, 2015)[11] of magnetite nanoparticles (JCPDS file No. 65-3107). The Debye-Scherrer equation is used for the analysis of the diameter of nanoparticles which are synthesised by the green synthesis method (Kero Jemal, B. V. Sandeep and Sudhakar Pola, 2017)[12]. From the results, the average particle size of the nanoparticles was found to be 91nm.

Debye-Scherrer equation ---------- (1)

$D = (0.9*\lambda) / (\beta* \cos \theta)$

Where; λ is the wavelength, β is the width of the base at half of its maximum intensity.

7.0 Conclusion

Magnetite nanoparticles were synthesised from lemongrass extract and characterized by XRD, and the patterns confirmed the phase composition and nature of the synthesised

8.0 Acknowledgement

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