Nano Adsorbents γ-Fe₃O₄ for Heavy Metal Pb (II) ion Removal

PRIYANKA R. PATIL

D. Y. Patil College of Engineering & Technology, Kolhapur

Abstract- Over the past decades, heavy metals are far away from wastewater by various purification processes like action, electro dialysis, precipitation, coagulation, etc. However, compared to the adsorption method, they need their limits, like low cost and low removal efficiency of trace heavy metal ion levels. Nano adsorbents are nanoparticles or Nano composites of organic and inorganic materials that have a high affinity for absorbing substances thanks to their small size and huge extent. Among the assorted kinds of nano adsorbents, Fe_3O_4, TiO_2, ZnO and their composites play a significant role. Recently, magnetic oxides, especially Fe_3O_4, are widely used as nano adsorbents for the removal of heavy metal ions.

Indexed Terms- heavy metals, Nano adsorbents, Fe_3O_4, metal oxides, etc

I. INTRODUCTION

Heavy metals from wastewater are removed using various treatment processes like action, electro dialysis, precipitation and coagulation, membrane filtration, flotation, and reverse osmosis [5]. However, compared to the adsorption method, they need their limits, like high cost and low efficiency in removing trace levels of heavy metal ions. Thanks to its low cost and large-scale applicability, many industries use adsorption for water purification. Adsorption is usually performed using atomic number 6, which adsorbs dissolved organic substances during water treatment [6]. To avoid the high cost of carbon, many inexpensive adsorbents are used and tested to get rid of heavy metal ions. Various adsorbents are used, including rice husk ash [7], sawdust modified sugarcane bagasse [8], modified flax screen [9], waste biomass, and waste activated sludge [10], chitosan [11]. Some researchers have investigated adsorbents that might be used for water treatment with higher performance and lower cost,

but there's little information on the regenerative capabilities for regeneration purposes. High regeneration costs would cause the uneconomical acquisition of adsorbents and consequently, the resulting wastes would constitute secondary environmental pollution. Therefore, it's necessary to explore a replacement efficient adsorbent with an oversized extent and low regeneration costs. Water treatment and purification require simple, effective, and cheap technologies that have the power to get rid of toxic contaminants. The event of latest nanomaterial's with increased capacity, selectivity, and affinity to heavy metals is thus an emerging and interesting area of research. Nano adsorbents are nanoparticles or Nano composites of organic/inorganic materials that have a high affinity for adsorbing substances thanks to their small size and enormous area. Nano adsorbents are designed to possess more reactive nanoparticles or nanostructured components that concentrate on specific contaminants and offer the likelihood of even greater adsorption capacities. Nano adsorbents are employed in air or water purification, moreover as in groundwater remediation or wastewater treatment processes. They need an oversized area available to react with pollutants and their small size provides greater mobility in order that they are often efficiently transported through groundwater. Additionally, nanoparticles maintain their properties for an extended time and don't seem to be littered with soil acidity, temperature, or nutrient levels, and might be effectively used for field-scale removal of heavy metals from wastewater. It's therefore a significantly improved remediation technology in terms of efficiency, selectivity, and specificity compared to traditional technologies. A series of efficient, cost-effective, and environmentally friendly nanomaterials with unique functions are developed for the potential detoxification of business wastewater, groundwater, surface water, and water. Among the assorted kinds of nano absorbents, oxide-based nano

adsorbents like Fe_3O_4, TiO_2, and ZnO and their composites play a significant role. Recently, magnetic oxides, especially Fe_3O_4, are widely used as nano absorbents for the removal of heavy metal ions like Ni^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Zn^{2+}, Co^{2+}, Cr^{3+}, and As^{3+} from wastewater [12]. As results of the large increase within the use of heavy metals in recent decades, it's led to an oversized removal of metallic substances within the aquatic environment. Industrial wastewater contains the next amount of heavy metals, which might pollute the water when released into nature. Industrial wastewater contains toxic heavy metals like zinc, arsenic, copper, nickel, mercury, cadmium, lead, and chromium, which are of particular concern during treatment. Heavy metals are elements that have over 5 times the particular gravity of water. Heavy metals are one in all the foremost toxic varieties of water pollutants. A minimum of 20 metals are considered toxic, and approximately 1/2 these metals are released into the environment in quantities that are hazardous to the environment and human health [13]. Wastewater containing heavy metals came mainly from electroplating plants, stabilizers, thermoplastics, pigment production, mining operations, fertilizer and pesticide industries, tanneries, batteries, paper industry, etc. These industries discharge wastewater containing heavy metals directly or indirectly into the environment. Because they're toxic and non-biodegradable, they have an inclination to accumulate within the living organism. Therefore, they cause variety of diseases and disorders. Zinc, copper, nickel, mercury, cadmium, lead, arsenic, and chromium are considered toxic metals of particular concern in wastewater treatment. Long-term exposure to arsenic through drinkable causes carcinoma and adversely affects the lungs, bladder, and kidneys. It also causes skin problems like changes in pigmentation and thickening (hyperkeratosis). Lead is another toxic metal pollutant that, when present in higher concentrations above 70 μg/dL within the blood (WHO) can damage the nervous and reproductive systems and kidneys and lead to high pressure and anemia. High amounts of zinc cause fever, cough, stomach pain, and fatigue, and high exposure results in cancer, which might even end in death. Large amounts of lead (>100 μg/dL) within the body can result in convulsions, coma, and death. In keeping with the EPA (US),

cadmium, when present in higher amounts than the tolerance limit, is dangerous and ends up in damage to human physiology and other biological systems. Exposure to cadmium around (1 mg/m3) may end up in several complications that may cause death [14]. Furthermore, electrolytically deposited maghemite nanoparticles were applied to get rid of lead (Pb) from wastewater.

II. COLUMN ADSORPTION STUDY

2.1 Chemicals:
All primary chemicals used for the experiments were of analytical grade. A stock solution of 1000 mg/L Pb(II) was prepared by dissolving 3.802 g of lead nitrate $[Pb(NO_3)_2]$ in 1.0 L of double-distilled water. Successive dilutions of the stock solutions were made to urge the specified concentrations of Pb (II) within the aqueous samples.

2.2 Experimental setup:
A glass column with a length of 30 and an inside internal diameter of 2.54 cm, filled with stuffed with a weighed amount of adsorbent was used as a fixed-bed adsorber. The column was filled with an adsorbent between two layers of insulator and a layer of glass beads the dielectric placed on the underside also acts as a filter aid. The adsorbent was added from the highest of the column and allowed to settle by gravity. The highest of the adsorbent was covered with glass beads to make sure the correct distribution of the inlet current. Synthetic wastewater was fed to the column by a peristaltic pump at a controlled rate of flow. Adsorption studies with Pb (II) adsorbate on γ-Fe_2O_3 were performed within the range of injection flow rates (15–25 ml/min), metal concentrations within the injection (10–30 mg/l), and adsorbent bed height (2–8 cm) at temperature and pH 4–6. Samples were taken from the column outlet and analyzed for copper employing a UV spectrophotometer (Systronics UV-106).

2.3 Effect of pH
The effect of fixing pH (3-7) on the adsorption of Pb (II) ions is studied. A rate of 1.0 mL/min and an initial Pb (II) ion concentration of 600 mg/L were maintained.

2.4 Influence of the initial concentration of Pb (II) ions.

Different initial concentrations of Pb (II) ions (150-550 mg/L) were used and also the effect on column performance was analyzed. The pH was maintained at 6 and also the rate of flow at 1.0 mL/min, respectively.

2.5 Effect of flow rate

Different flow rates (1-3 mL/min) were used and therefore the effect on column performance was analyzed. The initial inlet concentration was maintained at 550 mg/L at pH 6, respectively.

III. REPERCUSSION

3.1 Evaluation of Absorbance

The graph of absorbance dependence on concentration, i.e. the calibration curve, is shown in Figure 4.3. From the solution of different concentrations, 10 ml was taken, to which 2.5 ml of 1:1 ammonia was added and the absorbance was measured at a wavelength of $\lambda = 625$ nm.

Table 3.1 Evaluation of Absorbance

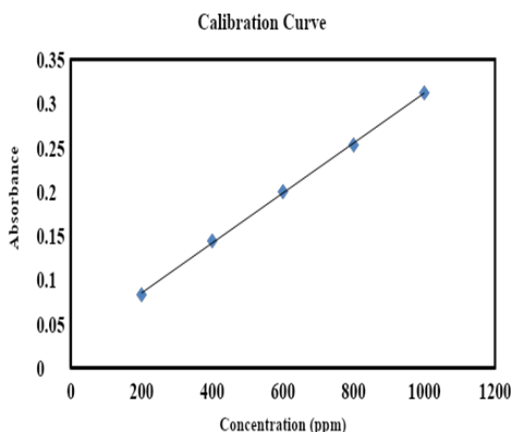| Concentration (ppm)	Absorbance
200	0.083
400	0.144
600	0.200
800	0.253
1000	0.312

Figure 3.1 Evaluation of Absorbance

The percent removal of metal ion from the sample was calculated using following equation

$$\% \text{ Removal} = \frac{C_0 - C_i}{C_0} \times 100$$

Where,

C_0 = Initial metal ion concentration (mg/L),

C_i = Final metal ion concentration (mg/L)

3.2 Outcome of pH

The outcome of varying pH (3-7) on the adsorption of Pb (II) ions, i.e., the removal efficiency at 25 °C, an initial Pb (II) ion concentration of 600 mg/L, and a flow of 1.0 mL/min, is shown in Fig. 4.5.. The capacity of an adsorbent to adsorb heavy metal ions depends on the chemical-physical properties of the adsorbent, the target metal ions, the hydrolysis capacity of the metal ions, and therefore the competitive adsorption of coexisting substances in solution. From Fig. 4.4 we will see that as pH increases, adsorption increases because metal ions (i.e., cations) tend to hydrate in a solution as pH increases. The increasing pH because of reducing competition between protons and metal cations and a discount in positive surface charge results in lower electrostatic repulsion between the surface and metal ions. Also, with a rise in pH from 5-6 because of the presence of OH- ions, adsorption increases. But at higher pH, pale white precipitate forms, and every one the lead ions settle out, so no adsorption experiments were performed at pH >6. However, at lower pH values, the presence of H+ ions ends up in repulsive forces between H+ and Pb+2 ions, leading to less adsorption.

Table 3.2 Outcome of pH on removal of Pb (II) ions

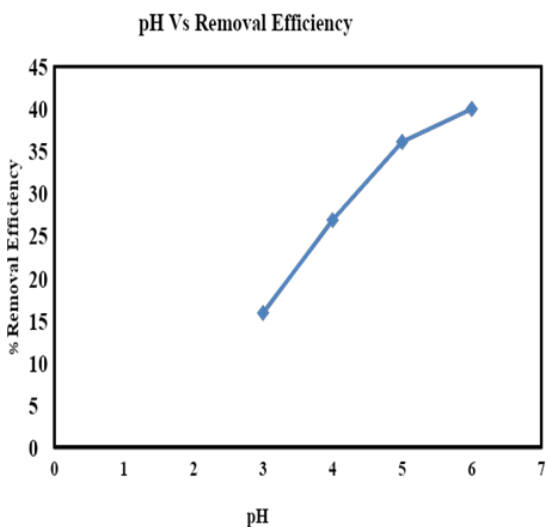| pH	Absorbance	% Removal
3	0.168	15.87
4	0.163	26.86
5	0.152	36.11
6	0.146	40.00

Figure 3.2 Outcome of pH on removal of Pb (II) ions

3.3 Outcome of initial Pb (II) ion concentrations
Different initial concentrations of Pb (II) ions (150-550 mg/L) were used and also the effect on column performance was analyzed. The pH and rate were maintained at 6 and 1.0 mL/min, respectively. a rise within the concentration of Pb (II) ions ends up in a rise in adsorption. Thus, the removal efficiency increases with increasing concentrations of Pb (II) ions, as shown in Figure 4.5. However, with further increasing concentrations, because of limited active sites, less adsorption occurs.

Table 3.3 Outcome of initial Pb ion concentration on removal of Pb (II) ions

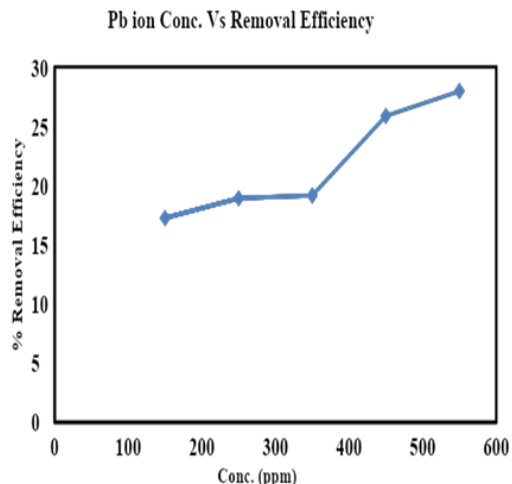| Concentration (ppm)	Absorbance	% Removal
150	0.081	17.24
250	0.105	18.91
350	0.128	19.14
450	0.139	25.86
550	0.140	27.96

Figure 3.3 Outcome of initial Pb ion concentration on removal of Pb (II) ions

3.4 Outcome of flow rates
Different flow rates (1-3 mL/min) were used and also the effect on column performance was analyzed. The initial inlet concentration and pH were maintained at 550 mg/L and 6, respectively. As seen in Figure 4.6, a lower rate of flow ends up in higher lead ion removal. At low flow rates, the number of your time spent within the influent, i.e. contact time, is more compared to higher flow rates, leading to higher adsorption. Thus, efficiency decreases with increasing flow. An extra increase in rate ends up in entrainment of the adsorbent.

Table 3.4 Outcome of different flow rates on removal of Pb (II) ions

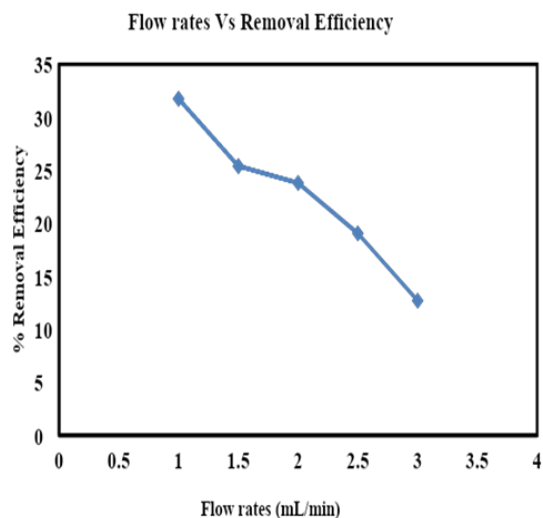| Flow rate (mL/min)	Absorbance	% Removal
1.0	0.140	31.74
1.5	0.148	25.39
2.0	0.154	23.80
2.5	0.167	19.04
3.0	0.175	12.70

Figure 3.4 Outcome of flow rates on removal of Pb (II) ions

Presumption:
1. Maghemite nanoparticles showed higher adsorption kinetics for Pb(II) compared to zero iron nanoparticles, which may be attributed to a better specific expanse.
2. Compared to other methods, electro deposition is commonly a cheap production method for the synthesis of nanoparticles with good controllability of size, shape, and crystallization.
3. Thus, these electrodeposited synthesized maghemite nanoparticles were used as an adsorbent for the removal of Pb(II) ions from aqueous solutions employing a fixed-bed adsorption column. The most removal efficiency was achieved at pH 6, Pb ion concentration 550 mg/l, and rate of 1 ml/min.

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