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Removal of toxic substances from zinc electroplating industry effluent using iron oxide nanoparticles

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Abstract
The objective of the present work was related to the removal of toxic substances from zinc electroplating industry effluent using iron oxide nanoparticles. Iron oxide nanoparticles were synthesized by chemical precipitation method and characterized using by SEM, EDAX, FTIR, and XRD. Physico-chemical parameters were estimated. Different quantities of Iron oxide nanoparticles such as 100,200,300,400,500 mg were employed for the removal of toxic substances from zinc electroplating industry effluent. SEM image of iron oxide nanoparticles was observed at the wave length range of 11.27, 10.86 band 11.28mm.EDAX spectrum recorded 3 peaks located between 2 and 10 ke V. The FT-IR spectrum of iron oxide nanoparticles was analyzed in the range of 400-4000cm^{-1}. XRD diffraction peaks are indexed as 30.22^0 (220), 35.53^0 (311), 43.25^0 (400), 57.14^0 (415) and 62.78^0 (440). All the parameters of Zinc electroplating industry effluent was decreased when treated with 500 mg of iron oxide nanoparticles.

Keywords: removal, toxic, zinc electroplating, industry, effluent, iron oxide nanoparticles

1. Introduction

Growing exploration of nanotechnology has resulted in the identification of many properties of nano materials such as enhanced magnetic, catalytic, optical and mechanical properties when compared to conventional formulations of the same materials [9]. These materials are increasingly used for commercial purpose such as fillers, pacifiers, catalysts, water filtrations, semiconductor, cosmetics, microelectronics etc [2]. Nanotechnology has been developed for the last decade and production of nano materials is one of the most attractive and practical aspects of science in the world. An emerging technology in water treatment is the use of nano adsorbents for and removal of radionuclides [25]. One of the main environmental applications of nanoparticles is the water sector. As fresh water become increasingly scarce due to consumption and contamination, scientists have begun to consider seawater as another source of drinking [15]. Heavy metals are the environmental priority pollutants and are becoming one of the most serious environmental problems and are produced and discharged from various industries such as electroplating, fertilizer, pesticide, metallurgy, and electric appliance manufacturing industries. Among different industries, electroplating industries release large quantity of toxic substances and heavy metals. Many methods such as precipitation, ion exchange, electro coagulation, floatation, adsorption etc are used for treatment of effluents. Among these, adsorption is one of the most applied and studied method in waste water treatment because of its low cost and ease to use. Traditionally agricultural wastes, activated carbon, zeolites, clays and many other meterials as adsorbents have been exploited by researchers but these are either having low adsorption or are not much effective when employed for actual industrial waste water treatment[19]. To solve and deal with this issue, the surface the focus shifted to utilization of nano materials as potential adsorbents for the removal of toxicants and metals because of better adsorption potential owing to high surface area and magnetic properties [5, 29]. Among nanparticles, iron oxide nanoparticles have long been used in the electronoic and chemical industries is becoming an increasingly popular method for treatment of toxic wastes and for remediation of contaminated water. The current research is one such effort aimed at treating zinc electroplating industry effluent. Hence the present study was carried out.

2. Materials and Methods

Ferrous chloride and sodium hydroxide was purchased from Lobachemia, India. All the reagents used for the synthesis of Fe_3O_4 were analytical grade and used without further purification. All the glass wares were washed thrice with deionized water and dried before use.

For the present study, zinc electroplating industry effluent was collected from Karisalkulam, Madurai, Tamil Nadu, India, in plastic containers, transported to the laboratory and stored for further use. Precipitation method was adopted for the synthesis of iron oxide nanoparticles. 150 ml of 0.03 M $FeCl_2$ was stirred vigorously using magnetic stirrer for 20 minutes. Precipitation was achieved by adding 100 ml of NaOH solution drop wise under vigorous stirring. The initial pH was observed as 3 and it was increased to pH 12 using 1 M NaOH. Then precipitating process was continued until dark black precipitate obtained. Then Fe3O4 precipitate was taken I to centrifuge tube and centrifuged at 1500 rpm for 20 minutes. The centrifugal process continued with water and two times with ethanol. Then the precipitate was dried and finally iron oxide nanoparticles were obtained. Synthesized iron oxide nanoparticles are characterized by using Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Spectroscopy (EDX), Fourier Transform Infrared Spectroscopy, and X-Ray Diffraction (XRD).

Physico-chemical parameters such as pH, electrical conductivity, total solids, total dissolved solids, total suspended solids, hardness, chloride, dissolved oxygen, sodium, potassium, calcium, COD, and zinc were estimated using standard methods [3]. Effect of different quantity (100,200,300,400,500mg) of iron oxide nanoparticles on the selected physic-chemical parameters of Zinc electroplating industry effluent such as pH, electrical conductivity, total dissolved solids, total hardness, chloride, COD, and zinc were estimated after exposing the effluent for 1 hour.

3. Results and Discussion

Fe_3O_4 nanoparticle was synthesized by chemical co precipitation method. Iron oxide nanoparticles can be synthesized through co-precipitation of Fe^{2+} and Fe^{3+} by the addition of a base. The size, shape and composition of iron oxide nanoparticles synthesized through chemical methods depend on the type of salt used, Fe^{2+} and Fe^{3+} ratio, pH and ionic strength [1]. A complete precipitation of Fe_3O_4 should be expected between pH 9 and 14 [10]. The precipitated magnetite is black in colour [7]. Fe_3O_4 produced are usually coated with organic or inorganic molecules during the precipitation process [14]. The morphology of the iron oxide nanoparticles were studied through scanning electron microscopy. It revealed the spherical and rectangular shapes of synthesized nanoparticles. It showed a clear image of highly dense iron oxide nanoparticles and micron scale size range about 9.48mm (scale bar at10µm) and 9.48mm (scale bar at 5µm)(Fig.1) The morphology and size of the nanoparticles and are usually characterized by SEM [24]. Iron oxide nanoparticles were more aggregate in post synthesis. The agglomeration can be avoided by doing the calcination process to get clear morphological structure and shape of particles [20]. The presence of carbon(C), oxygen (O) and iron (Fe) were revealed in synthesized nanoparticles by EDAX spectral analysis. EDAX spectrum recorded on the iron oxide nanoparticles is shown at three peaks located between 0.5 KeV and 6.5KeV.The two peaks of Fe element were located on the spectrum at 0.8KeV and 6.5 KeV and another peak of O element was located on the at 0.5 KeV (Fig.2). The EDAX spectrum iron oxide nanoparticles shown as three peaks located between 2KeV and 10 KeV [12]. The FTIR spectrum of iron oxide nanoparticles was analyzed in the range of 400-4000cm^{-1}. Fourier Transform Infrared Spectroscopy revealed the functional groups of iron oxide nanoparticles and viewed the functional groups of alcohol, phenol, alkanes, ketones, saturated aliphatic, alkyl halides and O-H, C-H, C-Br, C=O, C-I stretching of proteins.(Fig.3). Results of the present study are similar to other researchers [4, 8]. The XRD diffraction peaks indexed with crystal planes are 19.5º (111), 30.02º (220), 35.22º (311), 54.08º (422), 64.55 º (440) and 78.36º (444). The samples were scanned between angles 0º to 90º to obtain the equatorial reflection. Structure and crystalline size of nanoparticles were determined by XRD with JCPDS Card No.89-2355and 89-3854. The average crystalline size of chemically synthesized iron oxide nanoparticles were 15.58 and 21.34nm (Fig.4). Other researchers also reported that the synthesized iron oxide

Nano particles are crystal in nature and further confirmed by XRD and nano-crystal average size is 10 to 16 nm [27, 28]. The sharpness of XRD reflections clearly indicates that the synthesized iron oxide is crystalline. The physico-chemical parameters of zinc electroplating industry effluent are presented in table 1. The pH of the zinc electroplating industry effluent is 3. The same pH of 3 in electroplating industry effluent is also reported [21]. The electrical conductivity of the effluent was greater than the permissible limit of Bureau of Indian Standards (BIS)(300ms/cm).The total dissolved solids are 14800mg/l. The total solids in distillery effluent was 14600mg/l [23]. The total solids of electroplating industry effluent was 9700mg/l [22]. The total hardness level was comparatively higher than the BIS permissible limit of 250mg/l. Also reported higher total hardness (1912mg/l) in tannery effluent [16]. COD of the effluent was 1100mg/l exceeded the permissible limit of BIS (350mg/l).The COD of tannery effluent was above the accepted limit [23]. The chloride content in the effluent was 7600mg/l. Low value (197.38mg/l) of chloride in sugar industry effluent [13]. The sodium content of the effluent was 15.6 mg/l. The sodium content in sugar industry effluent was 125mg/l [11]. Potassium content in the effluent was 37.9 mg/l. The potassium content in paper mill effluent was 11.7mg/l [18]. Calcium content was 109mg/l and it is within the permissible limit of BIS (200mg/l). The calcium content in sugar industry effluent was 91mg/l [6]. The Zinc content in the effluent was 1324ppm. Other researchers reported higher (7348ppm) and lower (628. 83ppm) zinc content in electroplating industry effluent [26, 22] Effect of different quantity of iron oxide nanoparticles on the selected physico-chemical parameters of Zinc electroplating industry effluent is presented in table 2. The pH of the effluent increased to 6 when the quantity of iron oxide nanoparticles increased to 500 mg. The electrical conductivity, total dissolved solids, total hardness, chloride, COD, and zinc decreased with increased quantity of iron oxide nanoparticles. The COD of the industrial waste water was reduced when treated with higher quantity (4g) of iron oxide nanoparticles [17].

Table 1: Physico-chemical parameters of zinc electroplating industry effluent

S.No.	Parameters		Values
1.	pH		3
2.	Electrical conductivity	mS/cm	1000
3.	Total Solids	mg l^{-1}	14800
4.	Total dissolved solids	”	14600
5.	Total suspended solids	”	200
6.	Total hardness	”	1360
7.	Chloride	”	7600
8.	Dissolved Oxygen	”	6.70
9.	COD	”	1100
10.	Sodium	”	15.6
11.	Potassium	”	37.9
12.	Calcium	”	109
13.	Zinc	ppm	1324

All the values are averages of ten individual observations

Table 2: Effect of different quantity of iron oxide nanoparticles on selected physico-chemical parameters of Zinc electroplating industry effluent

S.No.	Parameters	Unit	Different quantity of iron oxide nanoparticles treated zinc electroplating industry effluent				
			100ppm	200ppm	300ppm	400ppm	500ppm
1.	pH		4	4.7	5	6	6
2.	Electrical conductivity	mS/cm	9000	8300	8000	7600	7000
3.	Total dissolved solids	mg/l	13600	12800	12400	12000	11500
4.	Total hardness	,,	1160	1000	980	800	600
5.	Chloride	,,	73OO	7000	6850	6500	6000
6.	COD*	,,	900	854	799	750	652
7.	Zinc	ppm	1220	1124	1015	875	712

COD* - Chemical Oxygen Demand All the values are averages of ten individual observations

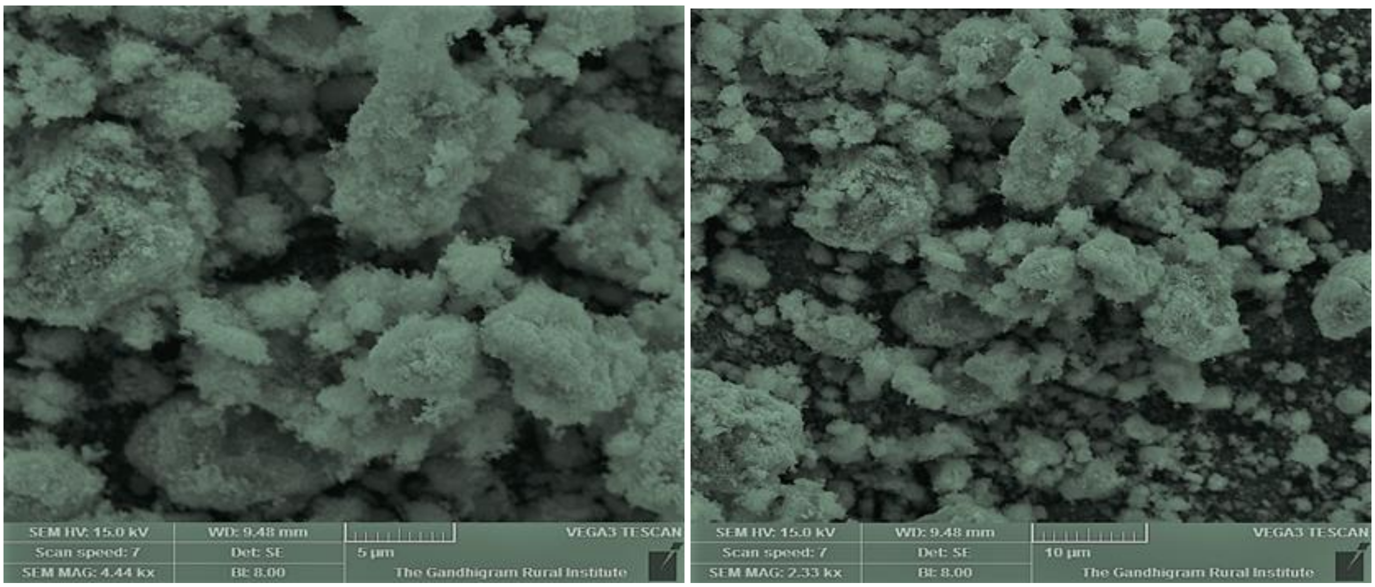

Fig 1: SEM Images of Iron oxide nanoparticles

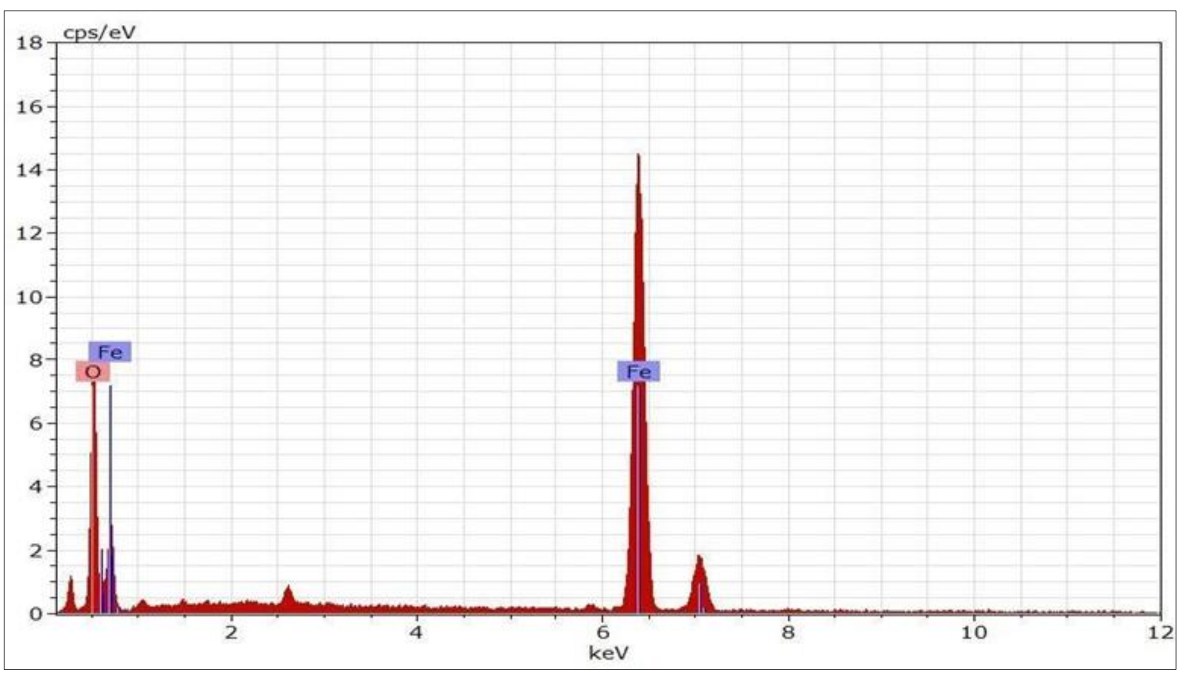

Fig 2: EDAX Image of Iron oxide nanoparticles

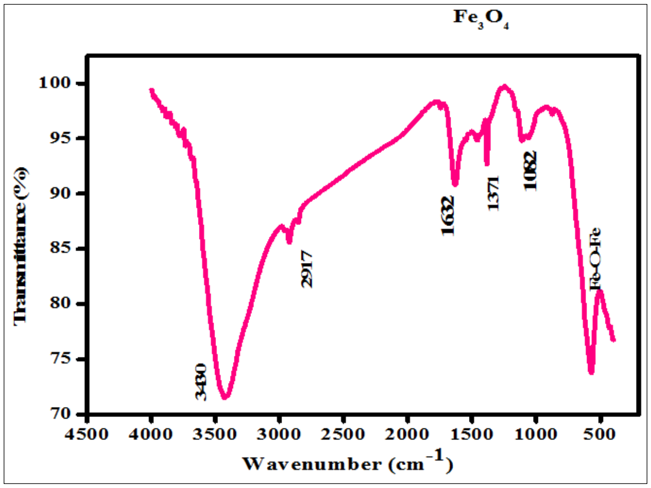

Fig 3: FT-IR Image of Iron oxide nanoparticles

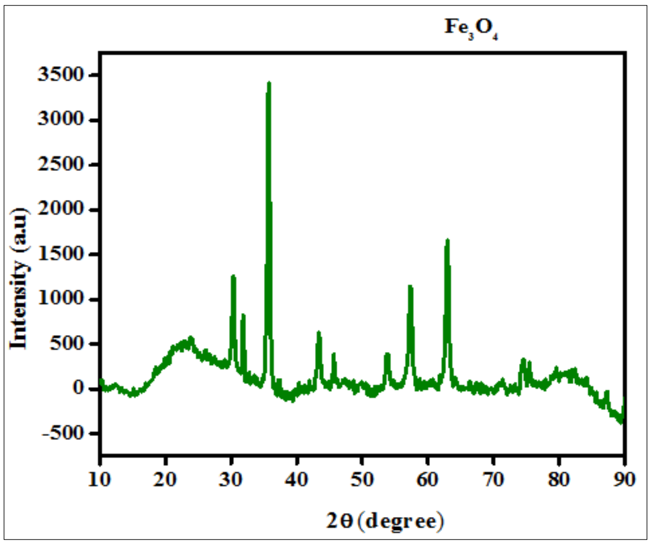

Fig 4: XRD Image of Iron oxide nanoparticles

4. Conclusion

Waste water from the zinc electroplating industry effluent was treated successfully by using iron oxide nanoparticles at a laboratory scale.

The result indicated that iron oxide nanoparticles were effective to reduce the electrical conductivity, total dissolved solids, hardness, chloride, COD, and zinc. Chemically synthesized iron oxide nanoparticles can be used for the removal of contaminants present in the electroplating industry effluent.

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