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Development of New Technology for the Removal of Cr^{6+} by Magnetic Nanoadsorbents from the Industrial or Sewage Wastewater

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Abstract

The heavy metals pose a serious water pollution problem especially contamination of portable groundwater with heavy metals that cause health hazards also its concentration is high in industrial and sewage wastewater. The main focus of this study to remove heavy metal chromium from contaminated water by using synthesized Iron Oxide Nanoadsorbent (ION). The batch adsorption study was conducted for the removal of chromium along with different parametric studies such Initial concentration of chromium metals, adsorbent dose, pH, contact time and temperature. The employed ION gives positive results, the adsorption of chromium is very rapid and most of fixation occurs at first 30 minutes. The adsorbent was characterized by before and after treatment of Chromium contaminated water, such as SEM-EDS, XRD and FTIR. The adsorption kinetics obeys second order kinetic. The result suggests that ION can be beneficial in chromium removal from the contaminated water.

1. Introduction

It is well known that, heavy metal ions and organic compounds remain a serious environmental problem facing the world for water pollution, as a result of their numerous industrial applications. In addition many of them are known to be toxic or carcinogenic even at low concentration, not biodegradable and tend to accumulate in living organisms causing a serious diseases and disorders [1]. Increasing quantities of chromium compounds have been used in anthropogenic activities and introduced into the environment as a consequence of its wide use in modern industries, mainly in electroplating and tanning factories. Therefore, their presence in water should be controlled. There exist three oxidation states for chromium in nature, Cr(II), Cr(III) and Cr(VI), however only the last two of species are stable [2,3].Cr(VI) is known to be highly mobile in soil and aquatic system, and is also 500 times more toxic, mutagenic and carcinogenic than Cr(III) [2,4]. The maximum permissible limit of for Cr (VI) in wastewater has been recommended as $0.005 mgl^{-1}$ by World Health Organization [3]. Conventional methods applied for Cr (VI) removal are mainly chemical precipitation, oxidation/reduction, filtration, ion exchange, membrane separation and adsorption Chemical precipitation produces great amounts of mud, while ion exchangers and membrane separation are relatively of very high cost [5,6].

The effluents from these industries contain chromium on its most common oxidation states on aqueous phase, Cr (VI) and Cr (III). These two Cr forms exhibit very different toxicity; Cr (III) is an essential nutrient required for sugar and fat metabolism, it has a very large safety concentration range, though large amounts of it can cause allergic skin reactions and cancer [7]. On the other hand, Cr (VI) is highly active and very dangerous due to its carcinogenic and mutagenic properties. Consequently, the removal of Cr (VI) from industrial wastewater has attracted much interest. Chemical treatment of chromium waste water is usually conducted in two steps [8]. In the first step Cr (VI) is reduced to Cr (III) by use of a chemical reducing agent. Sulphur dioxide, sodium bisulphate and sodium metabisulphite are commonly used as reducing agents. Following reduction of Cr (VI), sodium hydroxide or lime is added to the wastewater to precipitate Cr (III). This procedure produces large quantities of solid sludge containing toxic chromium compounds with high cost of disposal and even a possibility of ground water contamination [9]. There are a range of methods of producing metallic nanosized materials including radiation methods method consisting of reduction coupled with adsorption constitutes an eco-friendly and cost effective alternative to the existing treatments [10].

Different methods such as precipitation, ion-exchange, reverse osmosis, solvent extraction, electro dialysis techniques [11,12], biological treatments [13,14], membrane process [15-17], advanced oxidation process These methods are expensive, Other biomaterials containing weak basic groups such as not environment friendly of the waste. Therefore, the search for the first aspect is related to the wastewater treatment has been initiated, [18] and adsorption procedure [19, 20, 21] have been developed for the removal and recovery of metal ions and organic compounds from sewage and industrial wastewater. Amongst all the techniques proposed, adsorption-using sorbents is one of the most fascinating and popular methods for high quality treated effluents. Recently, a great attention and faster publications rate on developing cheaper and effective adsorbents containing natural polymers to overcome the non-biodegradability and high cost of the adsorbent resins were reported. Among these, polysaccharides, such as chitin and chitosan [22], cyclodextrin [23] as well as starch derivatives [24, 25,] deserve particular attention with respect to their ability to remove heavy metal ions from aqueous solutions.

Wastewater is considered one of the most important resources which could be a precious one if treated and managed well to be reused. However, in practice most of this domestic and industrial wastewater is discharged untreated or partially treated contaminated with a wide range of toxic chemicals and pathogens, causing serious drawbacks for human health and environment [26]. Recent findings show that nonmaterial's are highly promising in water purification process due to their unique properties like higher surface area per unit volume, ease with which they can be anchored onto solid matrices and the ability to functionalize with different functional groups to enhance their affinity towards target molecules [27]. A recent study by Subramanian et al. [28]. Regarding to chromium, there is a great amount of papers devoted to chromate anions biosorption by different kinds of organic materials. Recently, several authors [29–38] and specially the extensive work by Park et al. [39–42]. Iron oxide nanoparticles shows antimicrobial activity [43-48].

In this study magnetic nanoadsorbent (ION) were prepared by co- precipitation method which is very simple and no sophisticated instruments were required for synthesis. The main objective of this study is adsorptive capacity of magnetic for Cr^{+6} were high. The physical properties of the synthesized magnetic nanoadsorbent were investigated by SEM, EDS, XRD and FTIR for detection of different functional groups in present in the newly synthesized material. In order to better understanding of adsorption characteristic some kinetics model also were tested it gives positive results of chromium adsorption by synthesized ION.

2. Materials and Methods

2.1. Materials

All chemicals and reagents used for this experimental research were of analytical grade and used without further purification .for the synthesis of magnetic nanoadsorbent the precursor were used such as $FeCl_3.6H_2O$ and $FeSO_4.4H_2O$ supplied from the Loba Chemical Industries Ltd. The double distilled water was used throughout this proposed work were prepared by Distillation unit.

2.2. Synthesis of magnetic Nanoadsorbent (ION)

The synthesis of magnetic nanoparticles (ION) follows the reported methods with some minor changes and the detailed procedure of synthesis of Fe_2O_3 described as ,Take $FeCl_3.6H_2O$ and $FeSO_4.7H_2O$ in stochiometric amount were dissolved in double distilled water to prepare desired normal solutions, these solution are were mixed in 250 ml round bottom flask (R.B.F). The R.B.f placed in the water bath (LAB HOSP corporation Ltd.) and maintained the reaction temperature up to 358 K. with constant stirring for 30 minutes to get clear solution of mixed precursor. Add 25% liquid Ammonia in above clear solution drop by drop, because every drop of ammonia make the solution becomes colloidal, the magnetic particles are seen in the colloidal solution. The Co-precipitation reaction carried out at 358 K because if temperature increases which oxidize the Fe_2O_3 (ION) to Fe_3O_4. The Fe_3O_4 obtained at higher temperature which is energy and time consuming and required further instrumentation, some literature review shows for the synthesis of Fe_3O_4 require N_2 atmosphere which needed nitrogen cylinder and process becomes complicated. This experimental study focus to develop the sophisticated method for the synthesis of ION and also for the synthesis of Fe_3O_4 the excess amount of 25% liquid Ammonia is required. Therefore present reported investigation is superior as this experimental study is concert. The magnetic properties of synthesized magnetic particles were examined by the taking simple magnet nearby the R.B.F containing colloidal solution of magnetic particle, it is seen that the particles get attracted towards the magnet strongly, also that confirms the synthesized materials contain the magnetic properties as shown in Fig.1.

$$Fe^{+2} + Fe^{+3} \xrightarrow[\text{Liq.NH}_3]{\text{Co-precipitation}} Fe_2O_3 \text{.........................} \text{ Eq.1.}$$

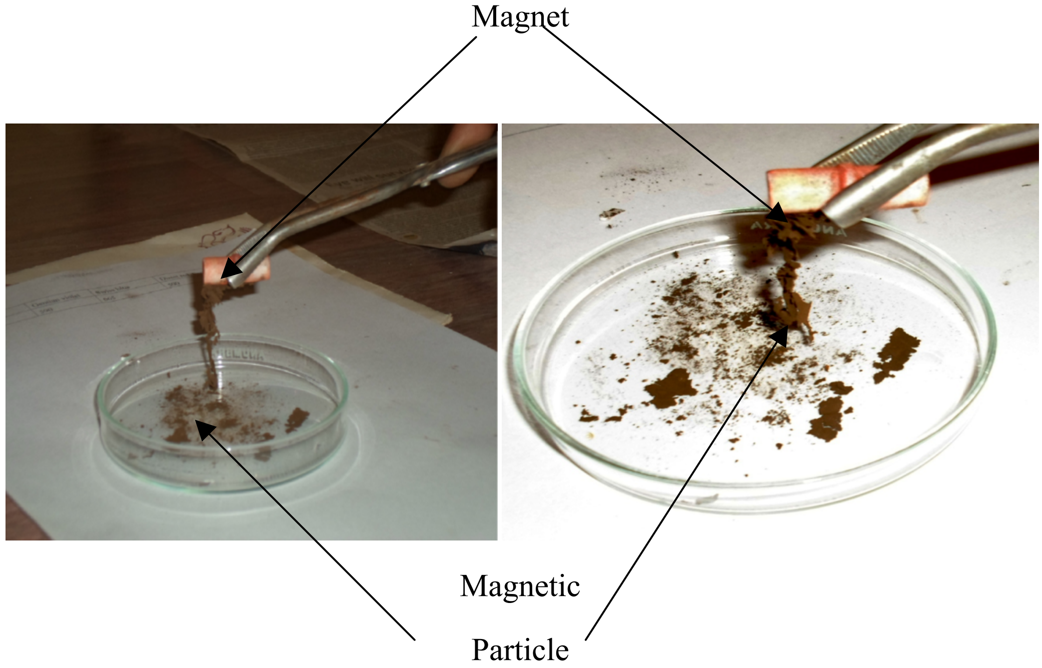


Figure 1: Showing synthesized Iorn Oxide Nanoadorbent magnetic properties.

2.3. Experimental Method

2.3.1.Batch Adsorption study

A stock solution containing Cr^{6+} prepared by dissolving a known quantity of $K_2Cr_2O_7$ (Potassium dichromate) in double distilled water, from this stock solution prepare desired ppm concentrations solution by dilution method. The batch adsorption studies were done by mixing 0.25 g of Magnetic nanoadsorbent with 50 ml of Chromium containing solution of various concentrations (10, 20, 30, 40 mg/L) in 100 ml glass beacker. The adsorption on ION nanoadsorbent was studied at pH 2 to 10 investigate the effects of pH values on the Cr^{+6} adsorption During this study the pH of the solution were adjusted by 0.1 M HCl and 0.1 M NaOH solutions. The pH value of the Chromium containing solution is stable throughout the study. All the adsorption study was carried out at room temperature 298K to 300K. A desired amount of synthesized ION were added to various concentrations of Cr^{6+} containing solutions at a particular pH and sample is placed on a magnetic stirrer (REMMI Motors Ltd. Mumbai) for a 15 minutes and then centrifuge it at 160 rpm for a 10 minutes .The supernant liquid was analyzed to determine the concentration of heavy metal by using Double Beam spectrophotometer (Systonics-2203).The different parametric study also carried out as follows. In present experimental research the adsorption capacity of (mg/g) for ION at 298K it was found that 7.2 mg of Cr^{6+} from wastewater containing 10 mg/L of Chromium.

2.3.2. Effect of Initial Cr (VI) concentration

The removal of chromium Cr^{+6} has been investigated in aqueous suspension of Fe_2O_3 as function of irradiation time. The rate of removal of Cr^{+6} ions was studied by varying the metal concentration from 50 to 10 ppm because for fixed adsorbent dose active sites remains the same, the number of substrate ions was accommodating the interlayer space increases so that removal decreases (Fig.2). This might be because of fact that with increase in initial concentration of the metal, more number of metal ions adsorbed on the surface of Fe_2O_3 .Thus increase in the several substrate ions accommodating in interlayer spacing inhibit the adsorption, which thereby decreases the reactive site of Fe_2O_3 result of that decrease in removal of chromium ions by Fe_2O_3 as the concentration of metal ions increases.

2.3.3. Effect of Adsorbent dose

An effect of ION on the removal kinetics of Cr^{+6} ions was investigated employing different dose of Fe_2O_3 (Iron Oxide Nanoadsorbent) the varying from 1 to 10g/L. The removal of Cr^{+6} increases rapidly with increasing the amount Fe_2O_3 as shown in Fig.3. The increase in the amount of ION increases the number of active sites on the Fe_2O_3 surface which turn increases the removal of Cr^{+6}.

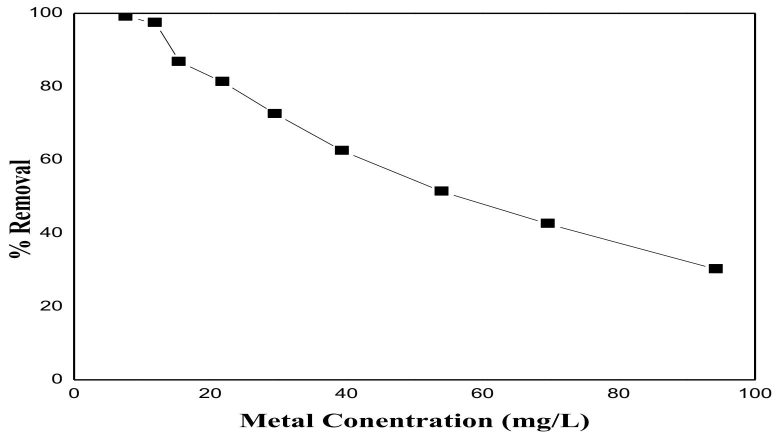


Figure 2: Effect of metal concentration on percentage removal of Cr^{+6} by Fe_2O_3 adsorbent dose 5g/L at pH 5.5.

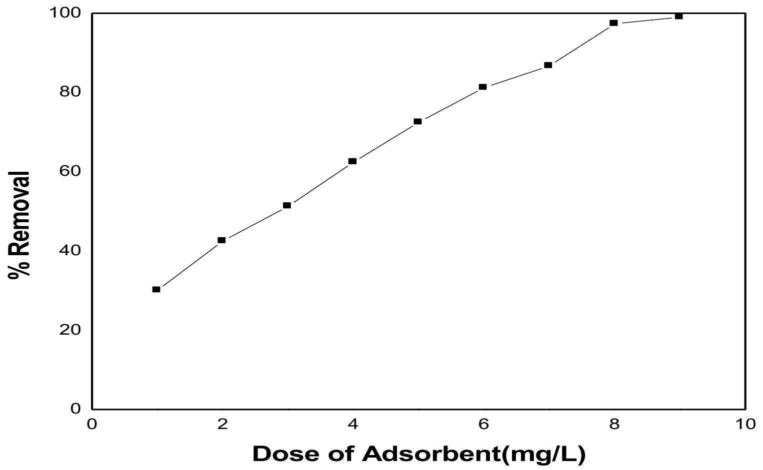


Figure 3: Effect of adsorbent dose on percentage removal of Cr^{+6} by Fe_2O_3 (ION) with contact time 150 min, pH 5.5

2.3.4. Effect of pH

The removal of Cr^{+6} was studied at different pH value as it was important parameter for reaction taking place on the particular surface .The role of pH on the removal of Cr^{+6} ion was studied in the pH range 4 to 10 at metal concentration 50 ppm and Fe_2O_3 concentration 5g/L Fig.4. It was observed that rate of removal increases with an increase up to pH 5.5. It was observed that the rate of removal of Cr^{+6} increases in the pH values up to 5.5 and beyond 6 this rate of removal became constant and then decreases gradually.

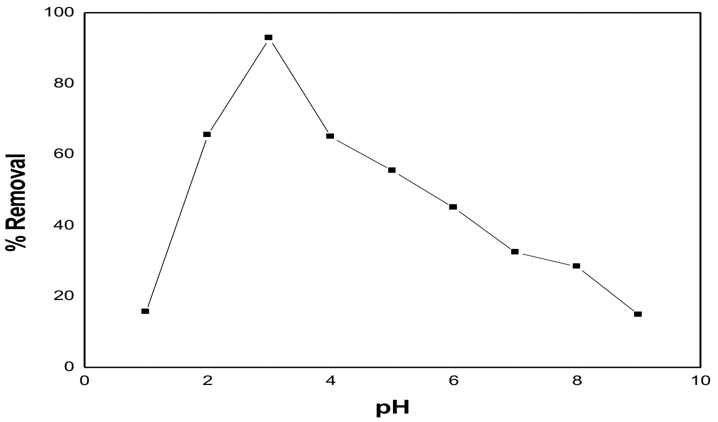


Figure 4: Effect of pH on removal of Cr^{+6} ion by Fe_2O_3 (ION) adsorbent dose 5g/L at 50 ppm metal concentration.

2.3.5. Effect of contact time

The effect of contact time for the removal of Cr^{+6} by semiconductor Fe_2O_3 as shown in (Fig.5).The Cr^{+6} was rapidly removed in the first 30 minutes and then adsorption rate decreased gradually and reached equilibrium in about 150 minutes. At the beginning adsorption rate was fast as the dye ions were adsorbed by the exterior surface of the Fe_2O_3 .When the adsorption of the exterior reached saturation the Cr^{+6} ions exerted onto the pores of the adsorbent Fe_2O_3 and were adsorbed by the interior surface of particle. This phenomenon takes a relatively long contact time

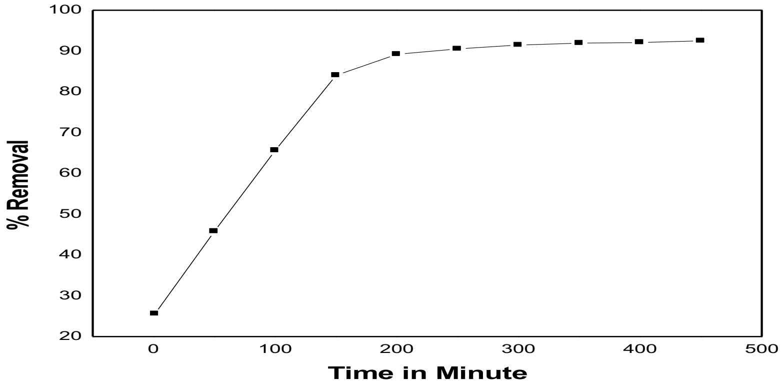


Figure 5: Effect of contact time of Cr^{+6} on percentage removal adsorbent dose 5 g/L, at pH 5.5.

3. Result and Discussion

3.1. FTIR

The prepared magnetic particles characterized by SEM (Scanning electron microscopy) to analyze morphological structure of magnetic material. The FTIR measurements were performed by using (Lambda Scientific FTIR -7600) with KBr background over a range of 4000-400 cm^{-1} to determine magnetic material.The Element detection was carried by EDS to examine % of elemental in synthesized magnetic material. I.R spectra obtained by FTIR with can be help in identifying the chemical composition or bonding present in newly synthesized molecule. The FTIR provides the tool that contains structural information about the presence of certain functional groups in the unknown molecule. The frequency at 3747.4cm^{-1} and 599.86 cm^{-1} indicates Fe-O bond. It clearly indicates that the unknown molecule is Fe_2O_3 as shown in FTIR graph Fig.6.

3.2. EDS Analysis of magnetic Nanoadsorbent

Elemental analyze of magnetic nanoadsorbent has been done using EDS. Existence of elements which are expected in structure of Fe_2O_3. In Table 1, a great deal of the Fe_2O_3 is adsorbed by Chromium ion. Thus, we can say that iron ions have been found in the structure of the Fe_2O_3 as shown in Fig.7.

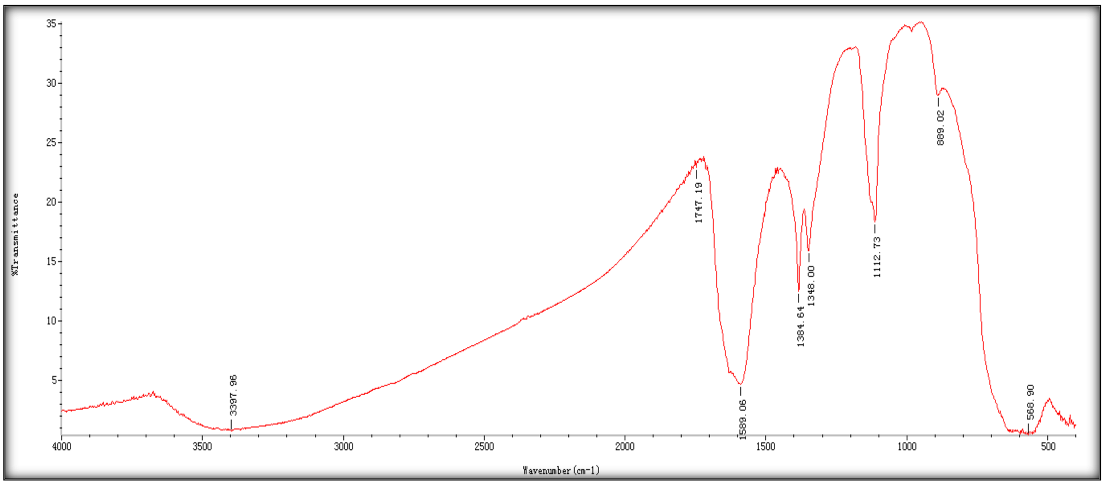
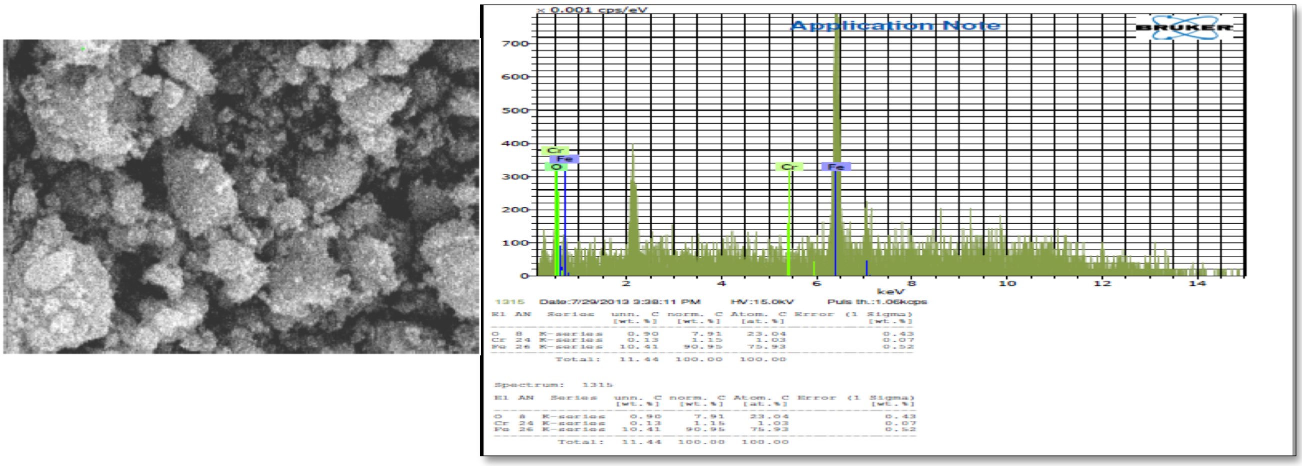


Figure 6: FTIR of Magnetic nanoadsorbent (ION) Showing different Functional group



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1315    Date:7/29/2013 3:38:11 PM      HV:15.0kV      Puls th.:1.06kcps
El AN   Series   unn. C norm. C Atom. C Error (1 Sigma)
                 [wt.%]  [wt.%]  [at.%]          [wt.%]
-------------------------------------------------------
O   8  K-series   0.90    7.91   23.04            0.43
Cr 24  K-series   0.13    1.15    1.03            0.07
Fe 26  K-series  10.41   90.95   75.93            0.52
-------------------------------------------------------
         Total:  11.44  100.00  100.00
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Spectrum:  1315

El AN   Series   unn. C norm. C Atom. C Error (1 Sigma)
                 [wt.%]  [wt.%]  [at.%]          [wt.%]
-------------------------------------------------------
O   8  K-series   0.90    7.91   23.04            0.43
Cr 24  K-series   0.13    1.15    1.03            0.07
Fe 26  K-series  10.41   90.95   75.93            0.52
-------------------------------------------------------
         Total:  11.44  100.00  100.00
```

Figure 7: EDS of Fe_2O_3 (ION) showing Elemental percentage.

Table 1: Percentage of elements and its elementary weight in synthesized Fe_2O_3 Nanoadsorbent.

Elements	**Elementary weight**
Fe	**75%**
O	**23%**
Cr	**2%**

3.3.SEM Analysis of magntic Nanoadsorbent

Scanning electron microscopy is widely used to study the morphological features and surface characteristics of adsorbent materials .The Fe_2O_3 was analyzed by SEM before and after adsorption of Cr^{+6}. The Fig.8 a) and b) & Fig.9 a) and b) show the SEM micrographs of Fe_2O_3 and Fe_2O_3 Cr^{+6} adsorbed respectively.

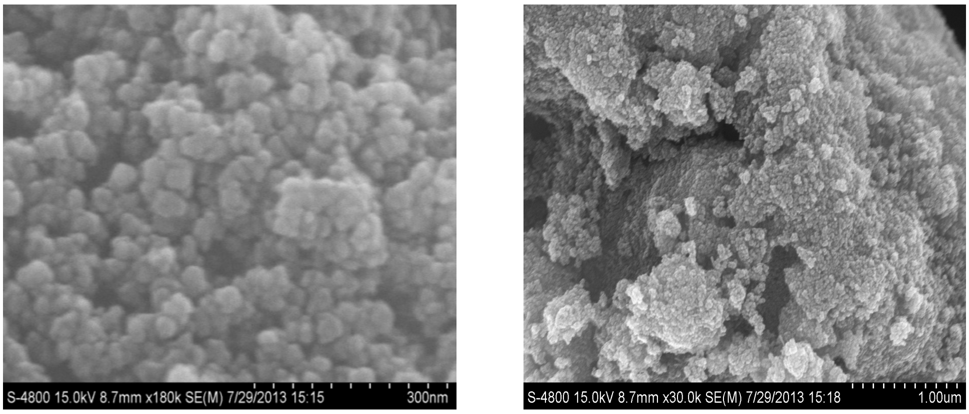

Figure 8: a) Before Adsorption b)After Adsorption

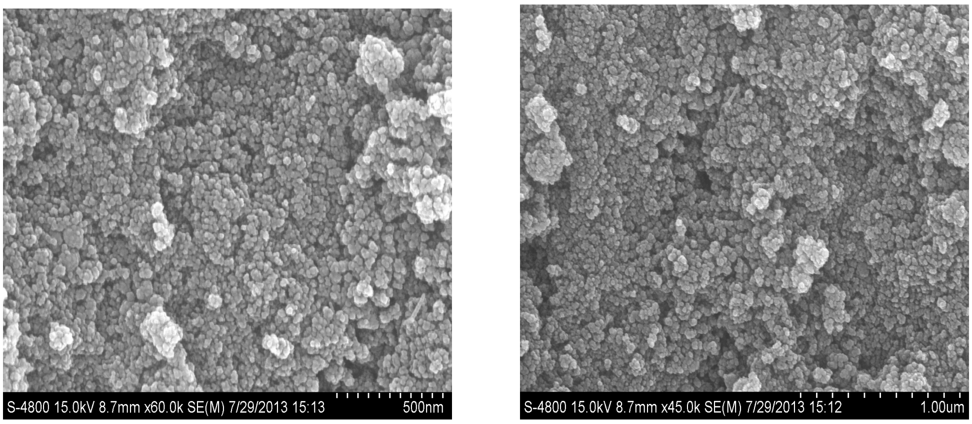

Figure 9: a) Before Adsorption b) After Adsorption

The iron oxide nanoadsorbent shows high surface area have geochemical properties which indicates the high potential of adsorption, therefore ION acts as the key nanoadsorbent for the removal of heavy metals from wastewater. They show surface texture and porosity of Fe_2O_3 with heterogeneous surface, microspores a mesopores as seen from its surface micrographs..

3.4. XRD Analysis of Iron Oxide Nanoadsorbent (ION)

The crystal structure and morphology of the iron oxide nanoadsorbent was characterized by X-ray diffraction at with high intensity CuKα 1 radiation (λ= 1.54060 A^0) with 2θ range from 10^0 to 80^0.as shown in fig.10. The XRD spectrum having main peaks at 2θ of 23.88^0 and 58.53^0. The low-angle X-ray diffraction analyses were performed to establish the presence of the crystalline phases in the system and to calculate the average crystalline from equation (2)

$$D = \frac{K\lambda}{\beta \mathrm{Cos}\ \theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Eq.2.}$$

Where *K* is a constant (K = 0.90), *D* is the mean crystalline dimension normal to diffracting planes, λ is the X-ray wavelength (λ=1.54060A^0) in radian, β is the peak width at half-maximum height, and θ is the Bragg's angle. XRD The calculated mean grain size D of crystallites for Fe_2O_3 (104) peak from the difractogram showed in fig.10 at an angle 33.58^0. By using above data, size of the Fe_2O_3 (ION) was calculated by Scherer's formula (Eq.2) 7.8nm.

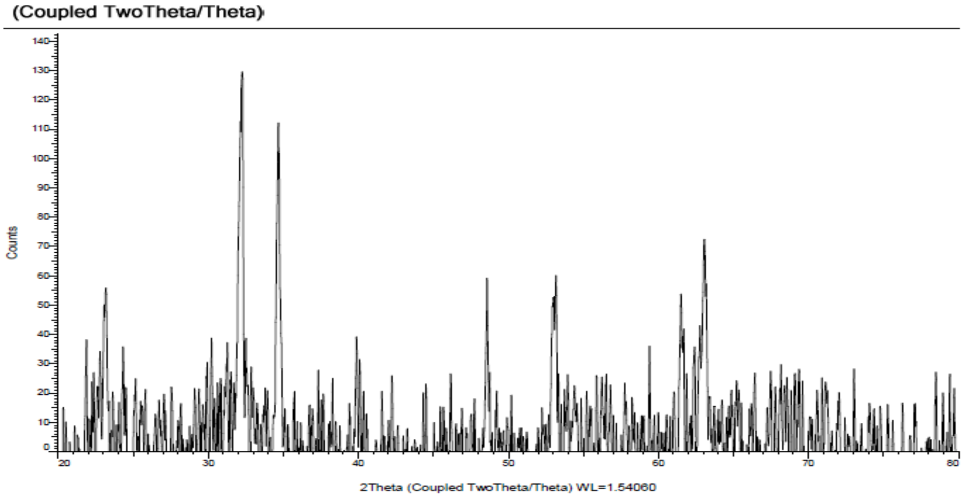

Figure10: XRD of Iron oxide Nanpadorbent (ION)

4. Adsorption Kinetics Study

4.1.Pseudo-first -order-model

The pseudo first order model was described by Lagergren [49],

$$\log (q_e - q_t) = \log q_e - \frac{k1^*t}{2.303} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Eq.3.}$$

The values of log (q_e - q_t) were linearly correlated with t. The plot of log (q_e -q_t) vs. t should give linear relationships from which the values of k_1 were determined from the slope of plot Fig.11.

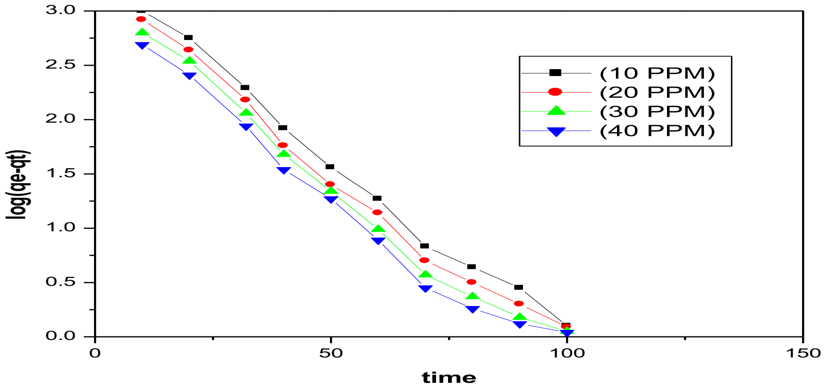

Figure11: Pseudo first order kinetics of Cr^{+6} ion with adsorbent dose 5g/L, at pH 5.5.

In many cases the first order equation of Lagergren does not fit well with the whole range of contact time generally applicable over the initial stage of the adsorption processes [50].

4.2. Pseudo-second–order-model

The pseudo second order-model is represented by the following equation,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{……………….Eq.4.}$$

The slope and intercept of plot of t/qt vs. t were used to calculate second order rate constant (k_2). The Fig.11.shows pseudo second order model, the values of equilibrium rate constant (k_2) are presented in table.2.

Table 2: Comparison of the pseudo first order and pseudo second order adsorption rate constants and calculated and experiments q_e values for different initial metal concentration.

Metal concentration/ppm	Adsorbent	q_e (exp)	first order kinetics		
			K_1	q_e(cal)	r^2
10	Iron Oxide Nanoadsorbent	3.81	0.078	3.8	0.966
30		3.75	0.057	3.73	0.963
50		2.88	0.054	3.7	0.958
Metal concentration/ppm			Second order kinetics		
		q_e (exp)	K_2	q_e (cal)	r^2
10		3.94	0.032	3.92	1
30		3.83	0.023	3.81	0.999
50		3.79	0.019	3.76	0.999

Table 3: Freundllich and Langmuir coefficients for adsorption of Cr^{+6} on Fe_2O_3 for different metal concentration and adsorbent dose of 1 to 5 g/L at pH 8 and contact time 30min.

Temperature	Freundlich coefficients				Langmuir coefficients			
	$K_{f\,(L/g)}$	n	1/n	R^2	Qo(mg/g)	b	R_L	R^2
299K	10.06	0.561	1.054	0.985	11.74	0.435	0.1865	0.996
309K	6.54	0.5998	0.654	0.993	36.11	0.129	0.2734	0.998
319K	3.311	0.7202	0.365	0.998	47.25	0.628	0.3543	0.99

5. Adsorption Isotherm

The equilibrium isotherm for the adsorption of Cr^{+6} by magnetic nanoadsorbent at pH 5.5 and 302 K. The equilibrium data were fitted by Langmuir and Freundlich isotherm equation [51,52]:

$Ce/qe = Ce/qm + 1/qm\,KL$ ……………………..Eq.5.

where *q*e is the equilibrium adsorption capacity of copper ions on the adsorbent (mg/g), *C*e the equilibrium copper ion concentration in solution (mg/L), *q*m the maximum capacity of adsorbent (mg/g), and *K*L is the Langmuir adsorption constant (L/mg) Fig.12.

The linear form of Freundlich equation, which is an empirical equation used to describe heterogeneous adsorption systems, can be represented as follows:

$\ln qe = \ln KF + 1/n \ln Ce$ ……………………..Eq.6

Where *q*e and *C*e are defined as above, *K*F is Freundlich constant (L/mg), and *n* is the heterogeneity factor. The values of *q*m and *K*L were determined from the slope and intercept of the linear plots of *C*e/*q*e versus *C*e Fig.13 and of values of *K*F and 1/*n* were determined from the slope and intercept of the linear plot of ln*q*e versus ln*C*e Fig.12. It was found that the correlation coefficients of Langmuir isotherm were 0.998 and those for Freundlich isotherm were 0.999 for Iron oxide magnetic nanoadsorbent revealed the data were fitted better by Freundlich equation than by Langmuir equation. Thus, the adsorption of chromium ions on the adsorbents obeyed the Langmuir adsorption isotherm.

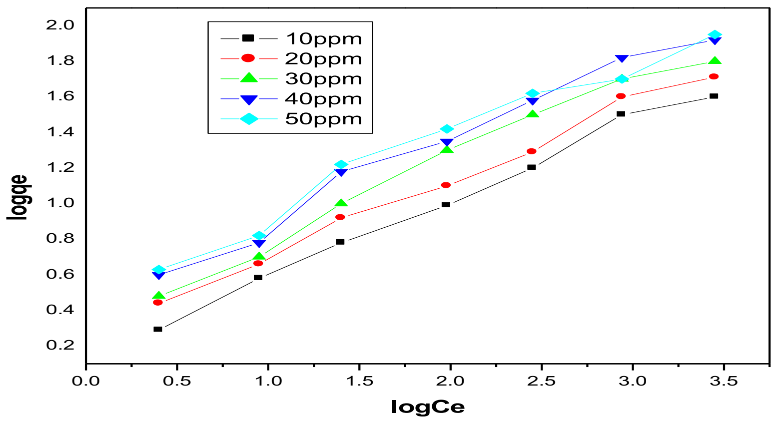

Figure12: Freundlich isotherm for Adsorption Cr^{+6} ions on ION.

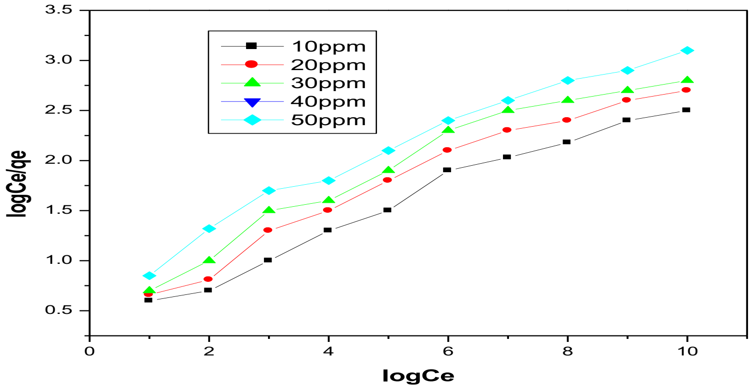

Figure 13: Langmuir isotherm for adsorption of Cr^{+6} on ION.

Conclusion

In this study a magnetic nanoadsorbent was synthesized by co-precipitation method is effective and eco-friendly and no sophisticated chemical and instruments were required. The magnetic nanoadsorbent prepare were employed for the adsorptive removal of heavy metals from industrial or sewage wastes. The adsorptive metals study shows positive results and obeys first order kinetics and adsorption study fit for the Langmuir and Freundlich model. Also other parametric study such as initial concentration, adsorbent dose, contact time, pH etc. shows effective adsorption. The present study shows that, Magnetic adsorbent can be used as an adsorbent for the removal of chromium from aqueous solution. The amount of chromium ion uptake (mg/g) found to increase with increasing contact time and the initial dye concentration, decrease with increasing adsorbent dosage. The rate of adsorption was found to confirm pseudo second order kinetics with a good correlation. Equilibrium data fitted very well in the Langmuir isotherm equation confirming the mono layer adsorption capacity of chromium ion on to magnetic nanoadsorbent with mono layer adsorption. The dimensionless separation factor (RL) called as equilibrium parameter showed that magnetic nanoadsorbent could be used for removal of chromium ion from
aqueous solution.

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