RESEARCH ARTICLE

ADSORPTION OF NICKEL IONS BY USING BINARY METAL OXIDES FROM AQUEOUS SOLUTION

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Manuscript Info	Abstract
Manuscript History: Received: 14 December 2015 Final Accepted: 16 January 2015 Published Online: February 2016 *Key words:* Co-precipitation, Fe-Ti and Fe-Mn, Adsorption isotherms, kinetics, Ni(II) **Corresponding Author* .... **M. Makeswari**	Binary metal oxides including Fe-Ti and Fe-Mn provide high surface area and specific affinity for heavy metal adsorption from aqueous systems. To date, it has become a hot topic to develop new technologies to synthesize metal oxides, to evaluate their removal of heavy metals based on modern analytical techniques (SEM-EDAX and XRD etc.). The present study mainly focuses on metal oxide preparation, physicochemical properties, adsorption characteristics and their application in Nickel removal. The effects of different condition for example solution pH initial metal ion concentration, contact time and adsorbent dose were studied by batch experiments. Maximum adsorption of Ni(II) was observed at pH 4 for Fe-Ti (54.01%) and Fe-Mn (67.78%) adsorbents. The equilibrium data of the adsorption was well fitted to the Langmuir isotherm. The adsorption process follows the pseudo-second-order kinetic model. The adsorption capacity of Fe-Mn was greater than that of Fe-Ti. According to the experimental results the adsorbent is expected to be an economical product for metal ion remediation of water and waste water.

Introduction:-

The widespread pollution of water with metals and metalloids is a high environmental and toxicological concern. The most toxic forms of these metals in their ionic species are the most stable oxidation states in which, they react with the body's bio-molecules to form extremely stable biotoxic compounds which are difficult to dissociate (Duruibe et al., 2007). Nickel(II) containing wastewaters are common as it is used in a number of industries including electroplating, batteries manufacturing, mining, metal finishing and forging. The Ni(II) concentration in wastewater from mine drainage, tableware plating, metal finishing and forging has been reported up to 130 mg/L (Patterson, 1985). Hence, removal of nickel from water and wastewater assumes importance.

Among various techniques available, adsorption was preferable considering the technological, environmental and economical constraints. Moreover, adsorption is universal and fast in nature and applicable for the removal of organic and inorganic pollutants even at low concentration.

In recent years the new promises that nanotechnology offers have spurred the industry to focus their research and investments on developing new applications such as purification of air, water and hazardous waste. Metal oxides have been widely used as adsorbents due to their unique surface characteristics than bulk materials and exhibit novel properties due to their small size. Recent studies have reported the removal of various contaminants using metal oxide adsorbents, including arsenic (Zeng et al., 2008; Banerjee et al., 2008; Tuutijarvi et al., 2009), chromium (Li et al., 2009), cadmium (Dong et al., 2007; Streat et al., 2008), dyes (Ada et al., 2009; Pirillo 2009), fluoride (Tripathy et al., 2006; Biswas et al., 2007; Biswas et al., 2009) and many others. Although research in the area of heavy metal removal by metal oxide is also underway, very little attention has been dedicated to this important issue.

In this work, a novel binary metal oxide such as Fe-Ti and Fe-Mn was prepared by the co-precipitation method with the aim of exploring its feasibility as adsorbent for the removal of nickel taken as a model toxic metal ion.

The objectives of this study are: (1) synthesis of Fe-Ti and Fe-Mn binary metal oxides by co-precipitation method and their characterization with respect to SEM, EDAX, XRD and pHpzc, (2) comparative batch adsorption study of the two for Ni (II) ions with respect to various environmental parameters, (3) comparative isotherm and kinetic studies. Adsorption studies were carried out as a function of effect of pH, contact time, adsorbent dosage, Initial metal ion concentration on the adsorption of Ni (II) ions. Based on these studies, the Langmuir, Freundlich, Temkin and Dubinin –Radushkevich isotherm models were used to fit the equilibrium data. Finally, the adsorption kinetics of these ions was evaluated by Pseudo-first-order, Pseudo-second-order, Intra particle and Elovich kinetic models.

Materials and Methods:-

Preparation of Fe-Ti and Fe-Mn binary metal oxides
The Fe-Ti and Fe-Mn binary metal oxide was used as absorbent in this study was prepared using a co-precipitation method by preparing the 3 molar solutions of ferrous sulphate (100 mL), titanium dioxide (100 mL) and manganese sulphate were weighed separately and dissolved in 100 mL deionized water, respectively. The solutions were then mixed in a water bath at a constant temperature of 80°C with vigorous magnetic-stirring, and the solution pH was strictly maintained in the range of 7-9. The suspension was continuously stirred for 3 h and aged at room temperature for 24 h. Then the suspension was filtered and washed with deionized water and dried. The absorbent precursor was finally calcinated at 300°C for 4 h, the obtained Fe-Ti and Fe- Mn binary metal oxide was stored and used for further experiments.

Adsorbate Preparation
The toxic heavy metal such as commercial grade nickel sulphate hexa hydrate was used as adsorbate in this study. A stock solution of $NiSO_4.6H_2O$ (1000 ppm) was prepared separately and suitably diluted accordingly to the various initial concentrations.

Characterization of the adsorbents
Physiochemical characterization of the adsorbents
Yield
The yield of the adsorbent in percentage was calculated by using the formula given below
$$\textbf{Yield } (Y) = (M/M_0) \times 100 \qquad \textbf{(1)}$$
where, M = Mass of the activated adsorbent, M_0= Mass of the adsorbent

Moisture content
About 200 mg of the adsorbent was weighed in a china dish and heated in an oven at $110\pm2°C$ for about 5 h. After heating, the dish was cooled in desiccators and weighed. Heating, cooling was repeated at 30 minutes interval until the difference between the two consecutive weighing was less than 5 mg. The loss in the weight gives the moisture content.
$$\textbf{Moisture content } (\%) = [(M-X)/M] \times 100 \qquad \textbf{(2)}$$
where, M = Mass of the materials taken for the test (g)
X = Mass of the materials taken after dying (g)

pH of the adsorbent
About 200 mg of the material was weighed and taken in 50 mL beaker. 30 mL of boiled and cooled water, whose pH was adjusted to 7.0, was added and heated to boiling. First 10 mL of the filtrate was rejected. The remaining filtrate was cooled and the pH was determined using digital pH meter 7007, Digisun Electronics.

Iodine Number
Iodine solution was titrated against sodium thiosulphate (A) with sample solution (B).
$$\textbf{Iodine value } = C \times \textbf{Conversion factor} \qquad \textbf{(3)}$$
where C = (B-A)

Determination of Zero Point Charge (pHzpc)

The zero surface charge of Fe-Ti and Fe-Mn were determined by using the solid addition method (Kumar et al., 2008). The experiment was conducted in a series of 250 mL glass stoppered flasks. Each flask was filled with 50 mL of different initial pH $NaNO_3$ solutions and 0.2 g of the adsorbents. The pH values of the $NaNO_3$ solutions were adjusted between 2 to 9 using 0.1 M HNO_3 or 0.1 M NaOH. The suspensions were then sealed and shaken for 2 h at 150 rpm. The final pH values of the supernatant liquid were noted. The difference between the initial pH (pH_0) and final pH (pH_f) values (pH = pH_0 - pH_f) was plotted against the values of pH_0. The pH equals to zero, yielded pHzpc of the adsorbent.

Surface characteristics of the adsorbent
Scanning electron microscopic spectroscopy (SEM)
SEM analysis of the adsorbents studied, were obtained using JEOL Scanning Electron Micrograph, was used to characterize the surface morphology and porosity of the adsorbents. A SEM can be utilized for high magnification of almost all materials. With SEM in combination with EDAX is it also possible to find out which elements are different in a sample.

Energy-dispersive X-ray spectroscopy (EDS or EDAX)
It is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on the investigation of an interaction of some source of X-ray excitation and a sample. It is used to make a quantitative chemical analysis of an unknown material. Inorganic elements can be analysed and it is possible to see how they are distributed in the material. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray Spectrum (Joseph Goldstein, 2003). It was done by using JED-2300 analysis station (JEOL).

X-ray refractory diffraction (XRD)
The adsorbent can be crystallographically characterized by means of X-ray diffraction (XRD). The adsorbents were exposed to Cu Ka radiation (k = 1.54060 A°) with the 2θ angle varying between 1° and 70°. The phases were identified by comparing the peak positions and intensities with those in the Joint Committee on Powder Diffraction Standards (JCPDS) data files.

Batch adsorption experiments
Batch adsorption experiments for individual samples were carried out to investigate the effect of different parameters such as adsorption dosage, adsorbate concentration; contact time and pH were studied. Batch adsorption experiments were performed by equilibrating 200 mg of the metal oxide adsorbents with 50 mL of 100 mg L^{-1} Ni (II) solution in sealed glass bottles. The samples were shaken at room temperature and aliquots were taken at appreciate time intervals as necessary and the concentration of Ni (II) were determined by using UV-2450 visible spectrophotometer. The maximum deviation observed was less than ± 4 %. The adsorption % and adsorbed amount (q_e) were calculated using the following equations:

$$\% \ of \ Removal \ = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (4)$$

$$q_e \ = (C_0 - C_e) \times \frac{V}{m} \qquad (5)$$

where C_o and C_e (mg/L) are the initial and equilibrium concentration of Ni (II) in aqueous solution, V is the aqueous volume (mL) and m is the weight of the adsorbent used (mg).

Adsorption kinetic studies
In order to investigate the potential rate controlling step of the Ni(II) adsorption process, the kinetic data were fitted to the four models, which were presented as follows in eqs 6-9 respectively, Ho, 2004; Ho and McKay, 1998; Gundogan et al., 2004; Elovich, 1959).

$$q_t = q_e \left(1 - e^{-k_1 t}\right) \qquad Pseudo \ first \ order \ kinetic \ model \qquad \textbf{(6)}$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 \, q_e^2} \qquad Pseudo - second - order \ kinetic \ model \qquad \textbf{(7)}$$

$$q_t = k_{id} t^{1/2} + C \qquad Intra \ particle \ diffusion \ model \qquad \textbf{(8)}$$

$$q_t = \frac{1}{\beta} \ln t + \frac{1}{\beta} \ln(\alpha\beta) \qquad Elovich \ model \qquad \textbf{(9)}$$

Where t is the contact time of adsorption experiment (h); q_e (mg/g) and q_t (mg/g) are respectively the adsorption capacity at equilibrium and at any time t; k_1 (1/h), k_2 (g/mg h), α (mg/g h), β (g/mg), k, m and k_{id} (mg/g $h^{1/2}$) are the rate constants for these models, respectively. Based on the R^2 results, the kinetics of Ni (II) adsorption on Fe-Ti and Fe-Mn can be satisfactorily described by either Power model or Elovich model.

Adsorption isotherm studies

The Equilibrium adsorption isotherms of Ni (II) onto Fe-Ti and Fe-Mn binary metal oxide were undertaken to understand the behaviour of the adsorbent at equilibrium conditions. Equilibrium data are basic requirements for the design of adsorption systems and adsorption models were used for the mathematical description of the adsorption equilibrium of the Ni (II) ion onto the adsorbent. The results obtained on the adsorption of Ni (II) ions were analysed by the well-known models given by (Langmuir, 1916; Freundlich, 1906; Tempkin and Pyshev, 1940; Dubinin, 1960). The linear forms of the four models are as follows:

$$\frac{1}{q_e} = \frac{1}{q_m k_L C_e} + \frac{1}{q_m} \qquad \qquad Langmuir\ isotherm\ model \qquad (\mathbf{10})$$

$$\log q_e = \frac{1}{n}\log C_e + \log K_F \qquad Freundlich\ isotherm\ model \qquad (\mathbf{11})$$

$$q_e = \frac{RT}{b_T} \ln K_T C_e \qquad \qquad Tempkin\ isotherm\ model \qquad (\mathbf{12})$$

$$\ln(q_e) = \ln(q_m) - K_{DR}\varepsilon^2 \quad Dubinin - Radushkevich\ isotherm\ model \quad (\mathbf{13})$$

$$\varepsilon = RT\ ln\left(1 + \frac{1}{C_e}\right) \qquad \qquad (\mathbf{14})$$

Where q_e is the amount of Ni (II) ion adsorbed onto the Fe-Ti and Fe-Mn binary metal oxide per gram at equilibrium (mg/g); C_e is the residual concentration of Ni (II) ion in solution at equilibrium (mg/L); q_m is the maximum monolayer adsorption capacity (mg/g); K_L is the Langmuir isotherm constant related to the affinity between the adsorbent and the adsorbate (L/g); K_F is the Freundlich coefficient showing the adsorption capacity $[(mg/g)(L/mg)^{1/n}]$; n is the heterogeneity factor; k_{DR} is the porosity factor $(mol^2 J^{-2})$; ε is the Polanyi potential; R is the Universal gas constant with a value of 8.314 J $mol^{-1}K^{-1}$; T is the absolute temperature (K); b_T is the adsorption potential of the adsorbent $(kJmol^{-1})$; and k_T is the equilibrium constant corresponding to maximum binding energy.

Results and discussion:-

Characterization of the adsorbents
The Physico - Chemical characteristics of the adsorbent

Physiochemical characteristics of binary metal oxide adsorbent were assessed and presented in the Table 1. The recorded values of yield, Iodine number, moisture content, pH, and pH_{zpc} for the studied adsorbent Fe-Ti and Fe-Mn was given in the Table 1. This result indicated that yield and iodine number can be correlated with ability to adsorb low-molecular-weight substances and provides a measure of surface area or capacity available to small molecules. The higher the yield and iodine value, the higher will be the adsorption ability of the adsorbents. The measure of moisture content has been reported that if the moisture content of the adsorbent is more, it dilutes the action of carbon and necessitates utilizing some extra load of carbon (Madhavakrishnan*et al.*, 2009). From the physiochemical characteristics of the adsorbents surface properties have been identified. This proves the adsorption ability of adsorbents and higher adsorption ability of Fe-Mn compared with Fe-Ti for the removal of Ni (II) from aqueous solution.

Table 1 Physico - Chemical characteristics of Fe-Ti and Fe-Mn.

Parameters	Fe-Ti	Fe-Mn
Yield (%)	53.74	55.75
Iodine Value (mg/g)	1328.29	1409.62
Moisture content (%)	0.1637	0.1069
pH	5.64	5.45
Zero point charge(pH_{zpc})	3.06	3.42

The pH_{ZPC} of an adsorbent is a very important characteristic that determines the pH at which the adsorbent surface has net electrical neutrality. The point of zero charge for Fe-Ti is found to be 3.06 and for Fe-Mn is found to be 3.42. At this pH both the adsorbent has no charge on it. Below this zero point charges, the adsorbent has positive charge

density and above this zero point charges the adsorbent has negative charges of both the adsorbents increased which favours the adsorption of Nickel (Janos *et al.* 2003).

Surface characteristics of the adsorbents
Scanning Electron Microscopic (SEM) studies
The Scanning electron microscopy was used to study the surface morphology and the pore size of the studied adsorbents. Fig. 1a and 1b, shows the SEM micrographs of binary metal oxide adsorbents before and after adsorption of Ni (II). As can be seen from the figures, the adsorbents exhibit many orderly and developed pore morphology. In metal oxide samples we found that the regular porous which are often concentrated in the small size fractions. SEM image clearly shows that finer binary metal particles are primarily spherical, whereas the coarser particles are mainly composed of irregular and porous particles in these adsorbents.
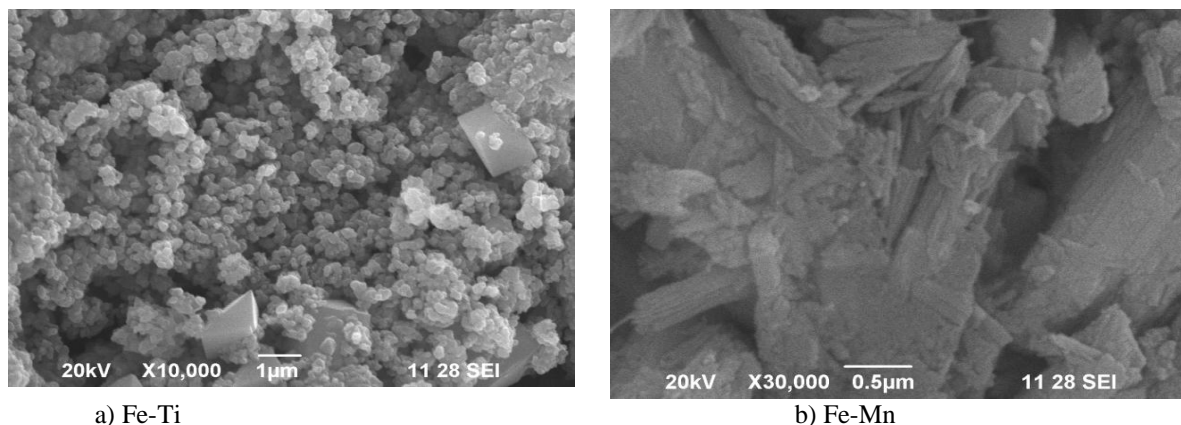

a) Fe-Ti   b) Fe-Mn
Figure 1 SEM images of (a) Fe-Ti and (b) Fe-Mn adsorbents.

Preparation of binary metal oxide and formation of new structures, play an important role in the heavy metal adsorption. SEM analysis was performed with the purpose to confirm the adsorption of heavy metals onto Fe-Ti and Fe-Mn binary metal oxide adsorbent surface.

Energy-dispersive X-ray spectroscopy (EDS or EDAX)
Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum. It was done by using JED-2300 analysis station (JEOL).

Based on the EDAX results, the elementary analysis of the Fe-Ti and Fe-Mn before adsorption of Ni (II) ions is presented in the Fig. 2a and 2b. The percentage mass of elements presented in the binary metal oxide are summarized in Table 2. From the percentage, we confirm the presence of Fe-Ti. In the Fe-Ti binary useful oxide, and Fe-Mn in the Fe-Mn binary useful oxide. It prove, by co-precipitation the binary metal oxides were prepared.
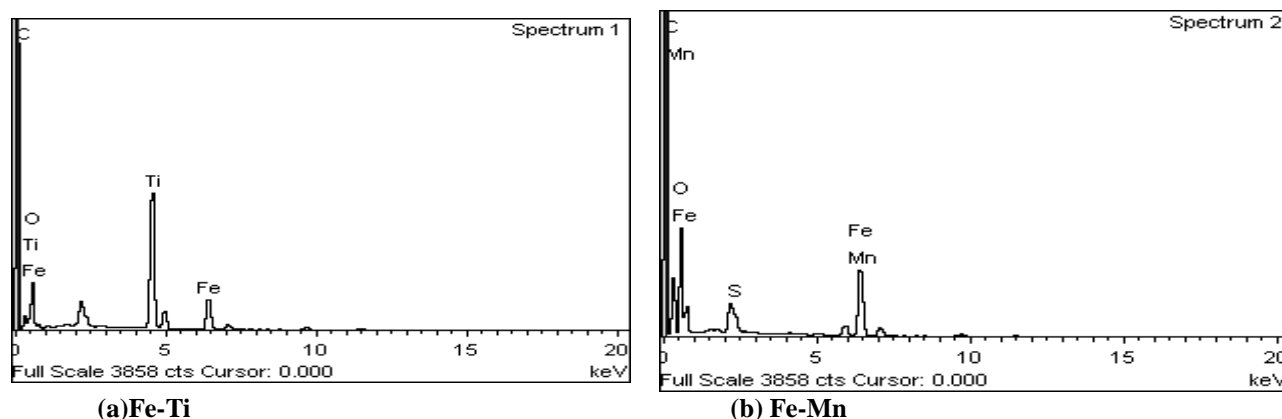

(a)Fe-Ti   (b) Fe-Mn
Figure 2 EDAX spectra of Fe-Ti and Fe-Mn adsorbents.

X-ray refractory diffraction (XRD)

The adsorbent can be crystallographically characterized by means of X-ray diffraction (XRD). The adsorbents were exposed to Cu K_α radiation (k = 1.54060 A°) with the 2θ angle varying between 1° and 70°. The phases were identifie d by comparing the peak positions and intensities with those in the Joint Committee on Powder Diffraction Standards (JCPDS) data files. The presence of Fe-Ti and Fe-Mn adsorbent was evident from the XRD patterns of binary metal oxide adsorbent for the adsorption of Ni(II) ions Fig. 3a and 3b. The XRD spectrum shows that the major components of binary metal oxide are Fe, Ti and Mn. Heavy metal removal on binary metal oxide is pH dependent in solution.

X-ray diffraction spectrum was obtained by using a Shimadzu XRD 6000 X-ray diffractometer. The prepared binary metal oxide samples were exposed to X-ray (k=1.5060 A°) with the 2θ angle varying between 10° and 80° with Cu Kα radiation. The applied voltage and current were 40kV and 30 mA, respectively. The phases were identified by comparing the peak positions and intensities with those in the JCPDS (Joint Committee on Power Diffraction Standards) data files.
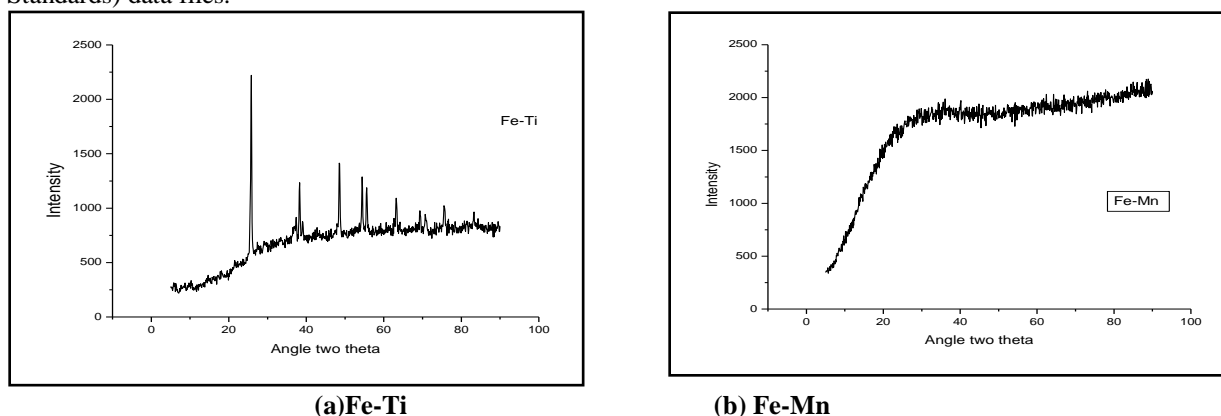

(a)Fe-Ti	**(b) Fe-Mn**

Figure 3 XRD results for (a) Fe-Ti and (b)Fe-Mn.

In Fig. 3a, peak at 29 in 2 θ scale corresponding to Ti oxide of peak between 40 and 50 in 2θ scale. Mn oxide Fig. 3b, 2 θ values corresponding to nano particle in XRD shown as peak at 45 in the 2 θ scale. Proved the presence of nano particles in both Fe-Ti and Fe-Mn.

Table 2 Data for the elements presented in Fe-Ti and Fe-Mn adsorbents.

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
Fe-Ti adsorbent					
C K	8.18	0.7309	9.78	0.72	18.06
O K	22.54	0.4431	44.45	1.18	61.63
Ti K	33.18	0.8978	32.29	0.79	14.96
Fe K	12.92	0.8373	13.48	0.54	5.36
Totals			100.00		
Fe-Mn adsorbent					
C K	27.72	0.7203	31.65	0.89	46.22
O K	42.08	0.8417	41.11	0.87	45.07
S K	0.67	0.9179	0.60	0.17	0.33
Mn K	3.20	0.8236	3.19	0.28	1.02
Fe K	23.85	0.8366	23.44	0.59	7.36
Totals			100.00		

Equilibrium adsorption studies
 Effect of solution pH on the adsorption of Ni(II) ions onto Fe-Ti and Fe-Mn Adsorbents
The zeta-potentials of the Fe-Ti and Fe-Mn particles in water were measured at different pH. It was found that the Fe-Ti and Fe-Mn particles are positively charged at low pH and negatively charged at high pH, having a point of zero charge (pH$_{zpc}$) at pH 3.06 for Fe-Ti and at pH 3.42 for Fe-Mn. Therefore, it can be expected that positively charged metal ions are likely to be adsorbed by the negatively charged adsorbent particles at a pH > ZPC for Fe-Ti and Fe-Mn (Tan et al., 2008; Wang et al., 2007; Yang et al., 2009).

One of the most important factors that, the adsorption of metal ions is affected by the pH of the metal solution. The pH affects both the adsorbent and adsorbate chemistry in solution. The experiments carried out at different pH shows that there was a change in the percent removal of nickel ion over the entire pH range of 2 to 10 shown in the Figure 4, pH is one of the most important parameters controlling the adsorption process. When the pH was lower than 3, the uptake went up sharply with the increase of pH. From the result it is evident that optimum pH of 4 is required for appreciable removal of Ni(II) ions and hence this pH is employed as an optimum pH for further studies. The obtained maximum Ni(II) ion uptake is 53.97 % for Fe-Ti and 67.78 % for Fe-Mn. The zeta potential results agree with the effect of pH on the adsorption of Ni(II) ions. Among these two adsorbents Fe-Mn metal oxide adsorbent has higher removal capacity than Fe-Ti adsorbent.
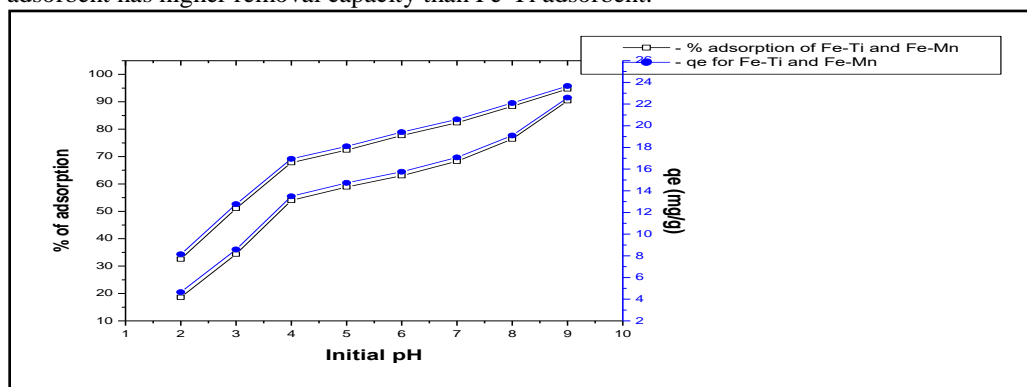

Figure 4 Effect of pH on the Adsorption of Ni(II) ions onto Fe-Ti and Fe-Mn adsorbents.

 Effect of contact time on the adsorption of Ni (II) ions onto Fe-Ti and Fe-Mn adsorbents
The kinetic experiments were performed by agitating the adsorbents Fe-Ti and Fe-Mn in bottles on shaking bath for 1.30 h at 30^0 C. In these tests, 200 mg of adsorbent per 50 mL of metal solution was used. The metal concentrations were determined at varying intervals. If we increase the contact time, the percentage of adsorption and maximum equilibrium adsorption capacity also increased for both the adsorbents. As shown, the rate of uptake of Ni (II) ion removal in the first 45 minutes was 54.01 % for Fe-Ti and 70.08 % in 45 minutes on Fe-Mn, and after this period, attained equilibrium. During the initial stage of adsorption, a large number of vacant surface sites are available for adsorption. After a lapse of some time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the adsorbate molecules on the solid surface. This was clearly shown in Fig. 5. Further, the attainment of maximum doping level within 45 minutes for both the adsorbents suggests that a very minimum contact time is sufficient enough for the removal of Ni(II) ions from water by these adsorbents. Among these two adsorbents Fe-Mn adsorbent shows higher adsorption capacity compared with Fe-Ti adsorbent.
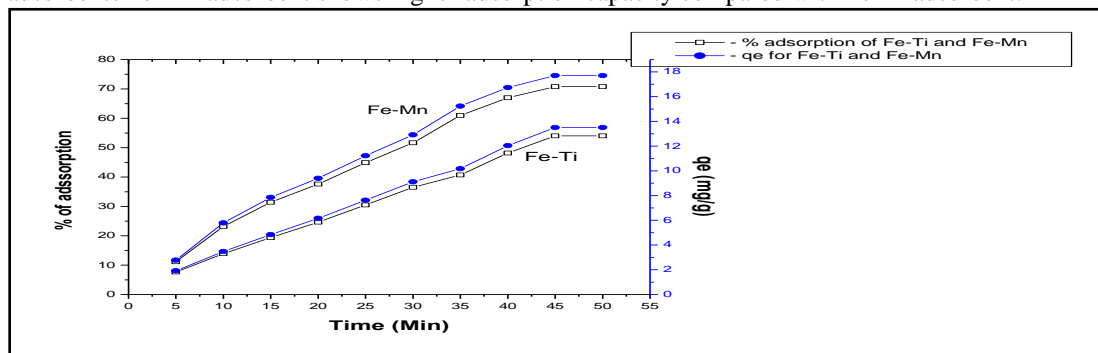

Figure 5 Effect of contact time on the adsorption of Ni(II) ions onto Fe-Ti and Fe-Mn adsorbents.

Effect of initial Nickel ion concentration on Fe-Ti and Fe-Mn adsorbents

The adsorption capacity is dependent on the initial metal ion concentration. The dependence of adsorption capacity of Fe-Ti and Fe-Mn binary metal oxide adsorbents on initial concentration of Ni (II) ion are shown in Fig. 6. As seen from fig.6, equilibrium uptake has been increased with increase in the initial metal ion concentration in the range of concentrations studied. The increase in adsorption capacity with an increase in initial metal ion concentration but the percentage of adsorption decreased with increasing the metal ion concentrations from 25 mg/L to 200 mg/L is a result of the increase in driving force due to concentration gradient developed between the bulk solution and surface of the metal oxide adsorbents. At higher concentration of metal ions, the active sites of Fe-Ti and Fe-Mn adsorbents were surrounded by much more metal ions and the process of adsorption continues, leading to an increased uptake of metal ions from the solution. Therefore, the values of q_e increased with the increase of initial metal ion concentrations (C_0).
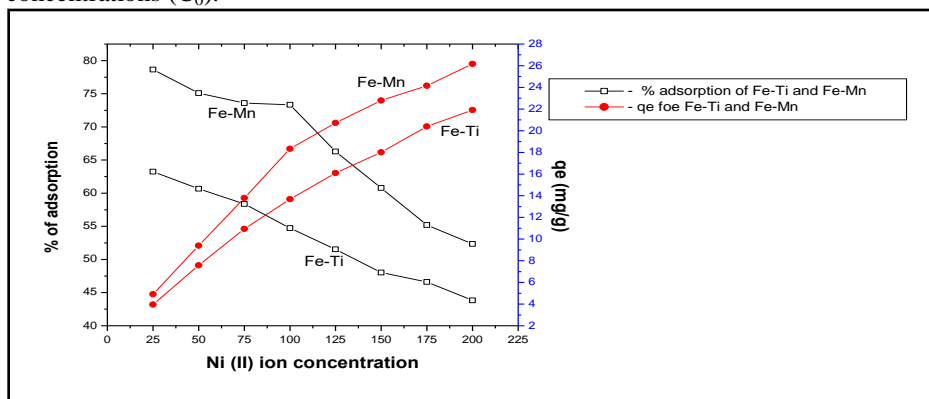

Figure 6 Effect of initial Ni (II) ion concentration on the adsorption of Fe-Ti and Fe-Mn adsorbents

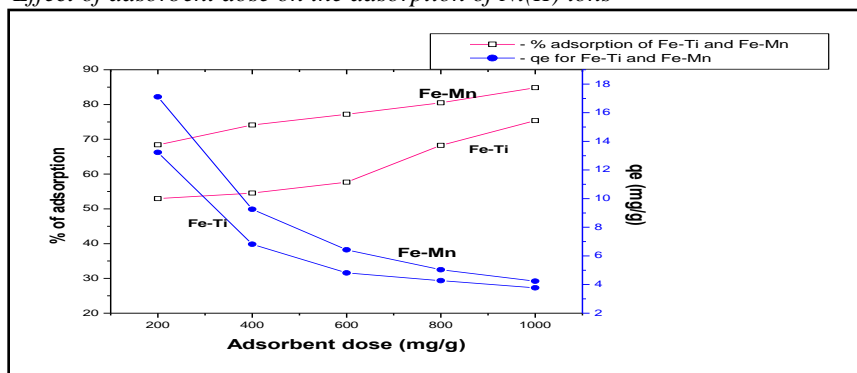*Effect of adsorbent dose on the adsorption of Ni(II) ions*

Figure 7 Effect of adsorbent dose on the adsorption of Ni (II) ions.

Different masses of the Fe-Ti and Fe-Mn binary metal oxides were chosen to study the effect of adsorbent dosage on Ni (II) ion adsorption. Results are shown in Fig. 7. The amount of Ni (II) adsorbed decreased (13.23 – 3.77 mgg^{-1} /50mL for Fe-Ti, 17.11- 4.24 mgg^{-1} /50mL for Fe-Mn) with increasing adsorbent dosage from 200 mg – 1000 mg but the percentage of adsorption (52.92 % - 75.36% for Fe-Ti, 68.43 % - 84.85% for Fe-Mn) increased with increasing the dosage of metal oxide adsorbents. This is due to the availability of higher number of Ni(II) ions per unit mass of adsorbents (Fe-Ti and Fe-Mn), i.e., higher Nickel ions/ adsorbent ratio. Thus, further experiments were carried out using 200 mg of adsorbent per 50 mL of Ni(II) ion solution, as it exhibits appreciable removal capacity, for the optimization of adsorption parameters.

Kinetic studies

The kinetic data for the adsorption of Ni(II) ions onto Fe-Ti and Fe-Mn adsorbents were tested with all the above discussed kinetic models and the parameters obtained from these models were tabulated in Table 3. The plots for pseudo second order kinetics for both the adsorbents are given in Fig. 8. By comparing the R^2 values of pseudo-first order and pseudo-second order kinetic models, it was evident that R^2 values of pseudo-second order kinetic model were closer to unity for both the adsorbents. Hence it was evident that the studied adsorption process can be better

studied with pseudo second order model. The linearity of pseudo second order equation for the kinetic data can be observed in Fig. 8. This implies that the adsorption of Ni(II) onto Fe-Ti and Fe-Mn was a chemisorptions process involving valence force through sharing or exchange of electron between adsorbate and adsorbent species (Bulut and Ozacar, 2008).
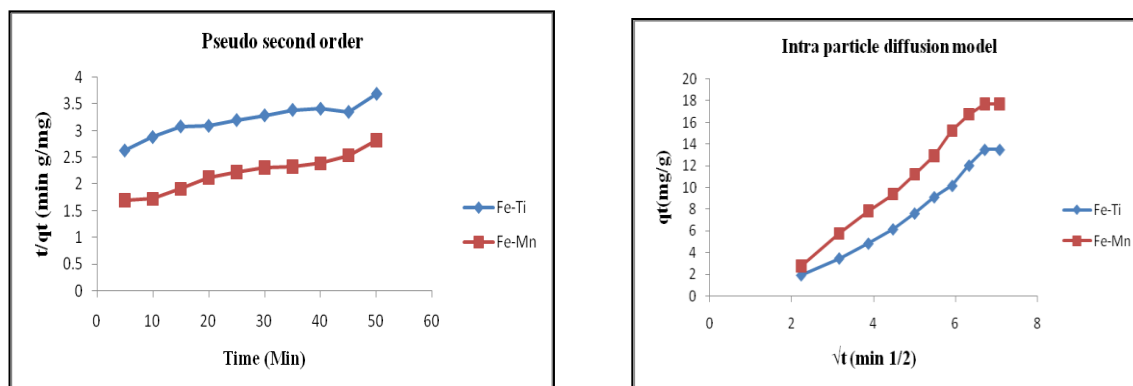

Figure 8 (a)Pseudo second order and (b) Intra particle diffusion kinetic plot for the adsorption of Ni onto Fe-Ti and Fe-Mn.

It is necessary to understand the mechanism of the adsorption process in order to use the adsorbent in industry level. To evaluate the mechanism of the process, the kinetic data were tested with intraparticle diffusion model and the plot was displayed in Fig. 8. If the intra particle diffusion is the sole process involved in adsorption, then the intraparticle plot should be linear and pass through the origin. But which is not the case in Fig. 8, it may be concluded that surface adsorption and intraparticle diffusion were concurrently operating during the NI (II) and the adsorbent interactions (Ho, 2004).

When the Elovich kinetic model was used, the linear coefficient for Fe-Ti was found to be 0.917 whereas it was 0.956 for Fe-Mn. The Elovich constant A_E for Fe-Tiwas 0.1855 mg/g min and A_E for Fe-Mn was 0.1433 mg/g min respectively. These values were also better for Fe-Mn than for Fe-Ti, which proves the suitability of the Elovich equation for Fe-Mn. This reveals that the presence of an intra-particle diffusion process in Fe-Ti and Fe-Mn.

Table 3 Comparison of the correlation coefficients of kinetic parameters for the adsorption of Ni (II) ions onto Fe-Ti and Fe-Mn adsorbents.

Kinetic Models	Parameters	Fe-Ti	Fe-Mn
Pseudo first-order	k_1 (min^{-1})	0.0507	0.0691
	q_e (mg/g)	18.0717	27.54
	R^2	**0.898**	**0.8887**
Pseudo-Second order	k_2 (g/mg/min)	0.0001	0.0003
	q_e (mg/g)	55.50	46.10
	h	0.6180	0.3719
	R^2	**0.938**	**0.902**
Intra particle diffusion	k_{dif} (mg/(g.min$^{1/2}$))	2.579	3.286
	C	4.72	4.777
	R^2	**0.980**	**0.990**
Elovich model	A_E (mg(g/ min))	0.1855	0.1433
	b (g/ mg)	0.4981	3.5265
	R^2	**0.917**	**0.956**

Isotherm studies
Table 4 illustrates the parameters of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms for the Ni (II) adsorption onto Fe-Ti and Fe-Mn. The R^2 values indicated that the Langmuir model fitted the data better than the

other three isotherm models (R^2 for Fe-Ti = 0.996 and for Fe-Mn= 0.951). The maximum monolayer capacity of Fe-Ti was 37.037 and Fe-Mn was 26.667. Therefore the equilibrium adsorption of Ni (II) ions onto Fe-Ti and Fe-Mn can be represented approximately by the Langmuir model. The correlation coefficients (Fe-Ti = 0.986 and Fe-Mn = 0.941) showed that the Freundlich model is comparable to the Langmuir model. The 1/n (for Fe-Ti = 0.0001 and for Fe-Mn is 0.0003) is lower than 1, indicating that Ni (II) is favorably adsorbed by the both the adsorbents.

Temkin isotherm model was used to determine the adsorption potentials of the adsorbent for adsorbates. The heat of Ni (II) ion adsorption onto Fe-Ti and Fe-Mn was found to be 345.46 and 33.19. The correlation coefficients R^2 obtained from Tempkin model were comparable to that obtained for Langmuir and Freundlich models, which explain the applicability of Tempkin model to the adsorption of Ni (II) ions onto Fe-Ti and Fe-Mn adsorbents. Dubinin-Radushkevich isotherm model was used to determine the characteristic porosity and the apparent free energy of adsorption. The values of E calculated using this model is 158.73 KJ/mol for Fe-Ti and 250 KJ/mol for Fe-Mn adsorbents, which indicating that the physico-sorption process plays the significant role in the adsorption of Ni (II) ions onto Fe-Ti and Fe-Mn adsorbents.
From the isotherm models tested for the adsorption of Ni(II) ions onto Fe-Ti and Fe-mn is fitted by the Langmuir is confirmed. It should be a monolayer homogeneous adsorption.

Table 4 Adsorption isotherm parameters for the adsorption of Ni (II) ions onto Fe-Ti and Fe-Mn.

Isotherm Models	Parameters	Fe-Ti	Fe-Mn
Langmuir	Q_m (mgg^{-1})	37.037	26.667
	b (Lmg-1)	0.0131	0.091
	R^2	**0.996**	**0.951**
Freundlich	1/n	0.0001	0.0003
	K_f (mgg^{-1})	55.50	46.10
	R^2	**0.986**	**0.941**
Temkin	α (Lg-1)	0.7405	0.3612
	β (mgL-1)	7.292	7.588
	b	345.46	33.19
	R^2	**0.983**	**0.983**
Dubinin-Radushkevich	Q_m (mgg^{-1})	16.387	20.210
	K (x10-5mol2kJ-2)	2.0000	0.080
	E(kJmol-1)	158.73	250.0
	R^2	**0.818**	**0.821**

Conclusion:-

The results of the monitoring studies carried out for the adsorption of Ni^{2+} from aqueous solution onto Fe-Ti and Fe-Mn adsorbents leads to the following conclusions. The Fe-Ti and Fe-Mn metal oxides were well prepared and it has great potential for application in removal of Ni (II) ions from aqueous solutions. The metal oxide adsorbents produced has high surface area. The present investigation shows the Fe-Mn is an effective adsorbent than Fe-Ti for the removal of Ni (II) ions from aqueous solutions. The surface morphology of the adsorbents was determined by analyzing through pH_{ZPC}, SEM-EDAX and XRD. Adsorption capacity of the adsorbents was highly dependent on the initial concentrations of metal ion, carbon dosage, contact time and solution pH. According to the pH_{ZPC} obtained for Fe-Ti and Fe-Mn, the pH of the adsorbate solution must be 3.06 for Fe-Ti and 3.42 for Fe-Mn adsorbents. So as to ensure that the surface of both the adsorbents will be more favorable for the adsorption of positively charged metal ions. The optimum pH corresponding to the maximum adsorption was found to be 4pH for both the adsorbents. The efficiency of Ni (II) ion adsorption increased with an increase in the adsorbent dosage, contact time but it decreases with increase in the initial concentration of the adsorbate solution. The adsorption data were well fitted by the Langmuir isotherm model; this is indicative of monolayer adsorption by Fe-Ti and Fe-Mn. Among the kinetic models tested, the adsorption kinetics was best described by the pseudo-second order equation for both the adsorbents. The adsorption process was found to be controlled by intra particle diffusion. The maximum

percentage of adsorption for Ni(II) ions, onto *Fe-Ti* was found to be 54.01% and for Fe-Mn was found to be 67.78 %. Among Fe-Ti and Fe-Mn, Fe-Mn shows most adsorption ability than Fe-Ti. The experimental studies showed that binary metal oxide (Fe-Ti and Fe-Mn) could be used as an alternative, inexpensive and effective material to remove high amount of Ni(II) ions from aqueous solutions.

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