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ABSTRACT
Nanotechnology is an emerging science offering promising models of decontamination. The present experimental design is to synthesize novel nanoparticles of Iron and Nickel oxides to be used as catalysts for in situ removal of different pollutants discharged from various industries. Particle size of synthesized iron and nickel oxides nanoparticles was characteristic of ~28-36 nm and ~48-56, respectively done with help of SEM and XRD analysis. Furthermore, the linkage of metal-oxygen linkage and red shift is confirmed through FTIR and UV-Visible spectroscopic technique, respectively. Physico-chemical characterization of industrial effluents showed remarkably higher concentration of nitrates and sulphates. Nitrates and sulphates were abundantly concentrated in leather industry effluents, designating it most polluted chemical processing industry. These results directed application of nanoparticles as adsorbents for selected removal of Nitrates and sulphates from wastewater in batch experiments. Concentration of the pollutants like sulphates and nitrates was reduced to 18 and 54 times, respectively, lower than the background concentration on application of Ni oxide nanoparticles. Kinetics model revealed pseudo second order whereas Langmuir and Freundlich equilibrium gave comparable fitness to adsorption data with regression coefficient of 0.999. The study concludes that nanotechnology provides potential and economically viable solution for removal of wastewater pollutants through synthesis of metal nano adsorbents.

Keywords: Nanotechnology; synthesis; wastewater treatment; emerging pollutants; adsorption; isotherms and kinetics

1. INTRODUCTION
Nanotechnology is an emerging science with wide applications in the remediation of environmental pollutants. In recent years, a great deal of attention has been focused on the synthesis and application of nanostructure materials as adsorbents or catalysts to remove toxic and harmful substances from water and air.

Resurgence to synthesize and manipulate nanoparticles finds use in improving air, soil and water quality in the environment. Reactive nanoparticles have a significant amount of surfaces and thus attract much interest to be applied as adsorbents in comparison to macromolecules. Various nanoparticles have been applied in removing radionuclides, adsorption of organic dyes, remediation of contaminated soils, and magnetic sensing. Metal oxides play a significant role in many fields of nanotechnology including nanocatalysis, sensing, supermagnetic properties, nanoenergy

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storage and conversion, fuel cells, and electroceramics (Bao et al., 2001; Gao et al., 2001; Braos-García et al., 2003; Liang et al., 2004; Seto et al., 2005; Tian et al., 2005; Jeon et al., 2005, 2006). The compounds and nanomaterials of iron and nickel having low dimensions have always been the subject of study due to their diverse applications in the fields of electronics, catalysis, magnetics etc. (Chen et al, 2009; Dominguez-Crespo, 2009; Libor and Zhang, 2009; Qiao et al., 2009; Masoud and Fatemeh, 2009; Kassaee et al, 2011; Somaye et al., 2011).

Synthesis is an important aspect of nanotechnology. An entirely new set of physical properties and applications of nanomaterials depends on the choice of selection procedure. Remarkable achievements in innovative synthetic routes and growth mechanisms have been made to obtain desired size crystal, morphology, microstructure and chemical composition. The sizes of nanoparticles are usually confined to less than 100 nm and such small sizes confer unique properties that are frequently different from the properties of bulk materials (Kannan and Sundaram, 2001; Zhuang and Wang, 2001), making them ideal for certain applications.

During synthesis of the nanoparticles control on nucleation and growth and agglomeration stages are the important stages which need to be controlled appropriately which is only possible by co-precipitation method. Co-precipitation method has been adopted to synthesize the metal oxide nanoparticles as it promise to provide not only smaller size particles as compare to solvothermal or hydrothermal method but also stable particles as well. Surfactant assisted method leaves the traces of surfactants on the surface of NPs causes unavailability of surface to the adsorbents due to which the efficiency is reduced (Bangash and Alam, 2004).

Various preparation techniques, such as sol-gel pyrolysis method (Sun et al., 2000), hydrothermal technique (Jing et al., 2006) and mechanical alloying (Ponder et al., 2000) has been used to prepare ferrite nanoparticles, but co-precipitation method is considered to be an economical way of producing fine particles (Hu et al., 2004; Ko et al., 2007).

The present study has two-fold significance. It offers simple synthesis method for metal and metal oxide particles and its application for the removal of pollutants like sulphates and nitrates from industrial wastewater. Structural properties of synthesized metal oxides are also investigated to understand the mechanism. Different kinds of adsorbents have been developed for the treatment of waste water (Kannan and Sundaram, 2001). Metal oxide particles enjoy a unique position having a significant amount of surfaces, thus, attracts much interest as potential adsorbents because of exclusive properties and potential application (Sun et al., 2000).

1.1 Objectives

- Synthesis of nanoparticles by different methods.
- Application of nanoparticles for removal of emerging pollutants from industrial effluent or waste water.
- Can nanoparticles be used for the selective removal of pollutants like sulphates and nitrates.
- Specificity of the nanoparticle with respect to specific pollutants.

2. MATERIALS AND METHODS

Nanoparticles were synthesized by using two different methods in order to check which method gives best yield and particle size of the adsorbents.

2.1 Synthesis of metal particles (Solvothermal direct method)

The Ni-bipyridine (sample 1) and Fe-bipyridine (sample 2) complexes were pre-
pared separately by a direct reaction between nickel chloride and iron chloride with 4,4-bipyridine following solvothermal method. Nickel chloride (0.1 mol) and 4,4-bipyridine (0.1 mol) were dissolved in 2-propanol (100 ml) separately. Then 4, 4-bipyridine solution was added drop wise to the metal salt solution. All chemicals were mixed with vigorous stirring, using a magnetic stir bar and refluxed at 80 °C for 10 hours and then cooled to room temperature. When the reaction was complete, greenish precipitates were collected and washed with dry ether of analytical grade several times to remove impurity. The final product was dried under vacuum at 60 °C overnight. Sample (b) was also synthesized in the same way with white precipitates. The grinded samples were then placed in argon fitted carbolite furnace for sintering. The samples were calcined under inert atmosphere, and then final product was dried.

2.2 Synthesis of metal oxide particles (Co-precipitation method)

Particles of Iron and Nickel were synthesized using co-precipitation method (Patricia et al., 1999; Chakrabarty et al., 2009). The procedure layout is as follows:

Acidic solution of 4.0mL of FeCl₃ and 1.0 mL of FeCl₂ (1:2 molar ratio, respectively) was thoroughly stirred for 10-15min followed by addition of 1.0M NaOH solution till the appearance of black precipitate. Strong magnet was used to settle the particles at the base of beaker and supernatant was discarded. Particles were kept in desiccators. Percentage yield was calculated to be 80%.

Nickel oxide particles were synthesized by drop wise addition of aqueous solution of NaHCO₃ (1.5 gm in 10 mL water) to the continuously stirring aqueous solution of NiCl₂ (2.3 gm in 10 mL distilled water). The precipitates obtained were centrifuged, washed repeatedly with distilled water and dried in oven at 100°C. Percentage yield of synthesized Ni particles is calculated to be 63%.

2.3 Characterization of adsorbents

The synthesized metal oxides particles were characterized with the help of FTIR (FTIR 8400, Shimadzu), UV-Visible (UV-1601 Shimadzu) spectrophotometer, SEM (JSM-6490A JEOL) and XRD (Model, Theta-Theta).

2.4 Batch adsorption

Time-dependent batch experiment was conducted for the study of adsorption of sulphates and nitrates and other compound using the synthesized materials. The following general procedure was used for a batch experiment.

The synthetic solution of sulphate and nitrate with known concentration (10 mg/L, 20 mg/L) was prepared at neutral pH. A known volume (10 mL) each was pipette into the series of cultural vial to which 1mg of the synthesized materials as adsorbent was added. Upon completion of the given contact time (in minutes) between adsorbent and adsorbate, the solution was filtered. The filtrate was determined with the help of UV spectrophotometer for metal nitrate and sulphate concentration. The standard Turbid-metric (4500- SO₄) and Ultraviolet spectrophotometric screening (4500-NO₃) methods are used for the sulphates and nitrates analysis (APHA, 2005). Each batch experiment was repeated with varying pH and induced concentration of metal salt solution.

2.5 Kinetics studies

In order to study the kinetics of the adsorption process, first order, pseudo first order, pseudo second order and intra particle diffusion equations were applied. The conformity between experimental data and the model predicted values is expressed by the correlation coeffi-
cient ($R^2$, values close or equal to 1). A relatively high $R^2$ value indicates that the model successfully describes the adsorption kinetics (Fadali et al., 2005).

### 2.6 Adsorption Isotherms

Adsorption equilibrium models of Langmuir (Langmuir, 1918) and Freundlich (Kalavathy et al., 2005) were applied to determine the relationship of sulphate and nitrate adsorption with different induced concentration. The best fitting isotherm was evaluated by linear regression, and the parameters (Lalhruaitluanga et al., 2010) obtained from the intercept and slope of the linear plots of these models.

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterization of adsorbents

The synthesized metal oxide particles were run on FTIR (FTIR 8400, Shimadzu) and UV-Visible (UV-1601 Shimadzu) spectrophotometer for characterization. FTIR spectrum of Fe$_3$O$_4$ is represents two absorption bands at around 592 and 630 cm$^{-1}$ which is due to the presence of Fe-O bond of Fe$_3$O$_4$ (Figure 1). Peaks at 2962 cm$^{-1}$ attributed to different C-H band vibrations, peaks appeared at 1261.49 cm$^{-1}$ is due to C-O stretching showing the absorption of atmospheric water and CO$_2$. FTIR of NiO shows the band in 700 to 800 cm$^{-1}$ range assigned to Ni-O stretching vibrations mode the broadness of band indicates that NiO powders are nanoparticles (Korosec et al., 2003) as shown in the Figure 1.

The broad absorption band centered at 3440 cm$^{-1}$ is attributable to the band O–H stretching vibrations and the weak band near 1635 cm$^{-1}$ is assigned to H–O–H bending vibrations mode. The jagged absorption bands in the region of 1000–1500 cm$^{-1}$ are assigned to the O-C=O symmetric and asymmetric stretching vibrations and the C–O stretching vibration, but the intensity of the band has weakened, which indicated that the ultrafine powders tend to strong physically absorption to H$_2$O and CO$_2$ (Qiao et al., 2009). FTIR spectrum of composite showed both the Fe-O and Ni-O bands.

![Figure 1 FTIR spectrum of Iron oxide Particles](image-url)
UV-VIS indicates blue shift in the bands which may be due to the presence of small sized nanoparticles, moreover according to Mie theory that absorbance increases in nanoparticles (Somaye et al, 2011). Metal clusters also show cluster size effects in optical spectra (Pinchuk et al, 2008).

A Scanning Electron Microscope (SEM) image of catalysts was characterized using Hitachi SEM SU-1500. The surface morphology and geometry of the metal nanoparticles studied by SEM and the result are presented here for Ni and Fe particles (Figure 2). The SEM image depicts the uniformity of the Nickel NPs with size range 150-250 nm. The SEM image of Fe iron particle at low resolution reveals the dispersion of Fe particle with relatively less uniformity and low size range 150-200 nm as well.

The typical SEM images of iron oxide and nickel oxide particles (Figure 3) show the non-spherical shape. From the image it is seen that a large number of particles are present and if we consider single one then calculated average size is to be nearly equal 36 and 48 nm for iron and nickel respectively.

However the SEM results (Figure 3a and 3b) showed the particles synthesized by adopting co-precipitation method show quite smaller size less than 100 nm (20-39.6 nm for Fe and 32-56.57 nm for Ni) as compared the metal particles synthesized by solvothermal method (Figure 2). Co-precipitation method is typical used and most preferred method for the synthesis of spherical smaller size NPs with high degree of uniformity.

The details XRD patterns of the NiO nanoparticles are shown in Figure 4. All the reflection peaks with relative intensities of different planes, indexed in the figure, specify the presence of NiO. The well crystalline nature of the prepared sample is easily being observed with the sharpness and the intensity of the peaks.

The XRD results (Figure 5) of the iron oxide nanoparticles indicated all the samples were in face centered cubic phase and in spinel structure according to the standard JCPDF file (card no-25-1402).

![Figure 2 SEM image of (a) Ni Particles and (b) Fe Particles](image-url)
Figure 3  SEM image of (a) Iron oxide particles and (b) Nickel oxide particles

Figure 4  X-ray diffraction pattern of Nickel oxide Particles
The present study is designed to devise a de-contamination model for the removal of nitrates and sulfates using synthesized materials. For this purpose synthetic batch experiments were designed separately for each material at optimum operating conditions described elsewhere (Imtiaz and Rafique, 2011). Series of Batch experiments were conducted. The variables used were (a) adsorbate concentration of 10 mg/L and 20 mg/L; (b) adsorbent mass of 1 mg; (c) pH 7 (neutral). However, the optimum concentration of the adsorbate was found to be 10 mg/L from adsorption experiments showing optimum removal of sulphates and nitrates.

All the plots throughout the manuscript are constructed on the data at optimum operating parameters of the experiment. It is concluded from the experiments that lower concentration of 10 mg/L of the adsorbate, 1 mg of the adsorbent dosage and the neutral pH are the optimum conditions for this study (Figure 6 showed the optimum concentration of adsorbate).

The results graphically presented in Figure 7 depict the efficiency of particles of nickel and Iron oxides for the removal of aqueous pollutants. Nitrates are removed to an optimum percentage of 58% and 67% on iron oxide and nickel oxide particles, respectively. The results are comparable to reported in literature (Li et al., 2008; Kasaei et al., 2011).

The sulfates removal was also attempted which shows a relatively lower percentage of removal efficiency. It is interesting to note that efficiency of both particles in removing sulfates is comparable in contrast to response for nitrates. However, on cumulative basis, it can be deduced from the results that nickel oxide particles are better candidate for the removal of both inorganic pollutants.

### 3.3 Kinetic studies

Different kinetic models including first order, pseudo first order, and pseudo second order and intra particle diffusion equations were applied to determine the mechanism involved in adsorption process.
The sorption kinetics may be described by a simple first order equation (Khan et al, 2007).

\[
\log Ct = \frac{k_1}{2.303} t + \log C_0
\]

The sorption kinetics may also be described by a pseudo first order equation (Ozacar, 2003). The integral form of the model is

\[
\log (q_e - q) = \log q_e - \frac{k_1}{2.303} t
\]

The adsorption kinetics may also be described by a pseudo second-order equation (Ho et al, 2001) the differential equation of this model is as follows:

\[
\frac{1}{q_t} = \frac{1}{k_2 q^2} + \frac{1}{q_e} \frac{1}{t}
\]

The intra-particle diffusion model is expressed as (Ayres et al., 1994)

\[
\log R = \log k_{id} + a \log(t)
\]
3.4 Adsorption isotherm model

Adsorption models of Langmuir and Freundlich were applied to determine the relationship of nitrates and sulfates adsorption with different induced concentration. The best-fitting isotherm was evaluated by linear regression, and the parameters obtained from the intercept and slope of the linear plots of these models.

Estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the nanomaterials was calculated using the Langmuir isotherm model since the saturated monolayer isotherm can be explained by the non-linear equation of Langmuir Equation:

\[
\frac{C_e}{q_e} = \frac{I}{q_{\text{max}}K_L} + \frac{C_e}{q_{\text{max}}}
\]

Freundlich isotherm is capable of describing the adsorption of organic and inorganic compounds on a wide variety of adsorbents (Kalavathy et al., 2005). The Freundlich equation is expressed as:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

The adsorption Isotherms and Kinetics is applied on the present study using Nickel and Iron particles as adsorbents for the removal of nitrates and sulphates. The data is summarized in Table 1. The higher R² values reveals that isotherms of Freundlich and Langmuir are in best agreement (R² = 0.999 for Nitrates and R² > 0.96 for Sulphates). The fitness of both Isotherms is also reported by (Hosik et al., 2009) for the adsorption of As (V) onto maghemite nanoparticles. Kinetic studies also stated that it follows the Pseudo second order which is supported by (Ho and Chiang, 2001; Wu et al., 2001; Hossain et al., 2005).

<p>| Table 1 Calculation of Parameters of Nitrates and Sulfates using Fe and Ni Particles |
|----------------------------------|-----------------|----------------|----------------|-----------------|-----------------|----------------|</p>
<table>
<thead>
<tr>
<th>Adsorption Isotherms</th>
<th>Metal Particles</th>
<th>Nitrates</th>
<th>Sulfates</th>
</tr>
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<tbody>
<tr>
<td>Langmuir</td>
<td>NN</td>
<td>K_L</td>
<td>-2.715</td>
</tr>
<tr>
<td></td>
<td>FN</td>
<td>K_L</td>
<td>0.3433</td>
</tr>
<tr>
<td>Freundlich</td>
<td>NN</td>
<td>K_F</td>
<td>-0.7184</td>
</tr>
<tr>
<td></td>
<td>FN</td>
<td>K_F</td>
<td>1.0963</td>
</tr>
<tr>
<td></td>
<td></td>
<td>q_m</td>
<td>-0.2715</td>
</tr>
<tr>
<td></td>
<td></td>
<td>q_m</td>
<td>0.7092</td>
</tr>
<tr>
<td>Kinetic Models</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st Order</td>
<td>NN</td>
<td>C_o</td>
<td>-0.0044</td>
</tr>
<tr>
<td></td>
<td>FN</td>
<td>C_o</td>
<td>0.6897</td>
</tr>
<tr>
<td></td>
<td></td>
<td>q_e cal.</td>
<td></td>
</tr>
<tr>
<td>Pseudo 1st Order</td>
<td>NN</td>
<td>K_1</td>
<td>4.8267</td>
</tr>
<tr>
<td></td>
<td>FN</td>
<td>K_1</td>
<td>-7E-07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>q_e cal.</td>
<td></td>
</tr>
<tr>
<td>Pseudo 2nd Order</td>
<td>NN</td>
<td>K_2</td>
<td>0.1483</td>
</tr>
<tr>
<td></td>
<td>FN</td>
<td>K_2</td>
<td>0.1705</td>
</tr>
<tr>
<td></td>
<td></td>
<td>q_e cal.</td>
<td></td>
</tr>
<tr>
<td>Intra-particle Diffusion</td>
<td>NN</td>
<td>a</td>
<td>1.8149</td>
</tr>
<tr>
<td></td>
<td>FN</td>
<td>a</td>
<td>1.7308</td>
</tr>
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</table>
CONCLUSIONS
The following conclusions are drawn from the present study:

- The synthesis procedure adopted offer simple, economical and efficient method for the preparation of Fe and Ni oxide particles of reduced size, percentage yield being 80 and 65, respectively.
- Co-precipitation method is better than solvothermal method for the synthesis of the spherical smaller size particle with high degree of uniformity.
- Nitrates and Sulfates are efficiently removed by Nickel oxide and iron oxide nano particles at optimum operating conditions of pH 7, induced concentration 10 mg/L and adsorbent mass of 1mg.
- Nickel oxide NPs are proved to be better candidate than Fe-oxide NPs.

FUTURE PROSPECTS

- Formation of thin membrane of the nickel oxide NPs which can be used in filters to capture inorganic pollutants like nitrates and sulphates from water.
- Ni-oxide nanoparticles can be used in small sachets or in form of pellets to remove the toxic pollutants efficiently at low level from water.
- Recyclable/regeneratable thin films on neutral or active support can be formed for filters
Ni-oxide nanoparticles can be dispersed homogeneously on the nano-support to get better efficiency.

REFERENCES


