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Symposium T: Advanced Magnetic Materials & Their Applications

Synthesis of Magnetic Iron-oxide Nanoparticle through Micro emulsion for Environmental Application

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Abstract

The magnetic iron oxide nanoparticles was synthesized by microemulsion with variation of process parameters . A microemulsion is prepared by dissolving AOT in iso-octane, followed by addition of 1butanol and then FeCl2 aqueous salt solution. The system has to be stirred slowly until a transparent micro emulsion suspension is formed. The same procedure was followed to prepare second micro emulsion that contains NaOH solution. This two micro emulsion system are mixed at a volumetric ratio of 1:1 and precipitation is formed. The particles are recovered, and washed with deionized water and acetone and dried. The whole synthesis exeresize are repeated for various changing process parameters such as w = [water]/[surfactant] mole ratio, change in surfactant, change in reactant concentration and change in oil chain length. The material so obtained is characterized and found to have in the range of 20-50 nm. The material is subsequently used to remove the arsenic from contaminated water and have 99 percent removal efficiency.

Introduction

Nanoparticles have versatile application because of their size-dependent chemical, physical, optical, electronic and magnetic properties. Iron-oxide nanoparticles have been used as: catalysts for environmental and energy applications (Chen and Yaacob, 2007), material nanocomposite (Nagy, 2006), drug delivery (Tartaj et al., 2003), magnetic resonance imaging (MRI) (Tartaj et al., 2003), pigment for paint industry and many more such application. There are various

synthetic route for the synthesis of such nano size (1-100 nm) particles such as: sol-gel processing, chemical co-precipitation, hydrothermal synthesis and microemulsion system. The specific properties of nanoparticles greatly depend on the size , shape which ultimately depends on the synthesis route (Eastoe, 2006). Microemulsion or the reverse micelles methods of synthesis for nanoparticles have certain potential advantage and have attracted much interest as compared to other reported methods (Zhang et al., 2004). The, water-in-oil (w/o) microemulsion or reverse micelles as represented in Figure 1, sometime called intelligent microreactors (Li et al 2009), has drawn much attentation in fabricating this magnetic iron-oxide nanoparticles. The w/o microemulsions consist of man-sized core water droplets , dispersed in a continuous oil medium which are stabilized by surfactant molecules as it contains both hydrophobic and polar hydrophilic groups and accumulated at the interface of oil/water system (Figure 1).

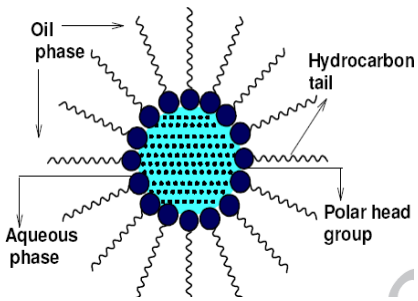


Figure 1: A typical structure of reverse micelle

Only few studies are reported on the synthesis of iron-oxide via w/o microemulsion system (Chen et al., 2009) . It is reported that the first magnetic nanoparticles formed in micelles were from the oxidation of Fe^{2+} salts to form Fe_3O_4 and c-Fe_2O_3 (Ahmad Malik, 2010). Eastoe (2006) It is also reported that there are five main properties of a microemulsion system which influences the size and polydispersity:1. the type of solvent employed,2. the surfactant or co-

surfactants used, 3.addition of electrolyte, 4.concentration of reagent and most controversially and 5. the molar ratio w = [water] / [surfactant].

Fluoride related health hazards are major environmental problem in many regions of the world. Literature review reveals that, India is among the 25 nations around the globe, where health problem occurs due to the consumption of fluoride contaminated water. In India, 17 states have been identified as epidemic for fluorosis and Odisha is one of them. The fluoride contamination in Odisha is wide spread, where 10 district out of 30 have excess of fluoride in ground water. Fluoride is a necessary micronutrient both for human and animal depending on the total amount ingested. More than 60% of our fluoride demand is fulfilled by the consumption of drinking water. Thus fluoride present in the drinking water can have beneficial or detrimental effect depending on its concentration and consumption of total amount. Excess of fluoride (>1.5 mg/L) in drinking water is harmful to the human health. The physiological effects of fluoride upon human health have been studied since the early part of 20th century. Several reports and studies established both the risk of high fluoride dosing and the benefits of minimal exposure. A low dose of fluoride was deemed responsible for inhibiting dental caries while a higher daily dose was linked to permanent dental and skeletal fluorosis.

Material and Methods:

Magnetic Ironoxide nanoparticle was synthesised by microemulsion technique: A microemulsion was prepared by dissolving AOT in iso-octane, followed by addition of 1butanol and then $FeCl_2$ aqueous salt solution. The system was stirred slowly until a transparent microemulsion suspension is formed. The same procedure was followed to prepare second microemulsion that contains NaOH solution. This two microemulsion system was mixed at a volumetric ratio of 1:1

and precipitation was formed. The whole synthesis exeresize was repeated for various changing process parameters. After the addition of both the microemulsion, immediately a dark green precipitate was formed which after some time transformed to black. The particles were recovered and then washed several times with distilled water and acetone. It was dried at room temperature.

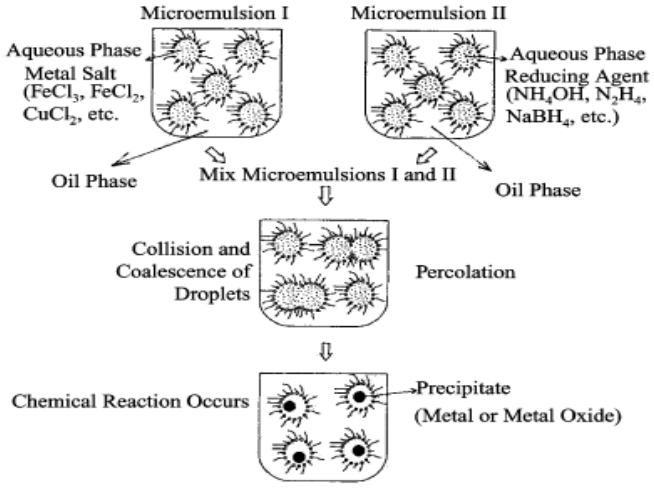


Figure 2 Mechanisms for the formation of metal particles by w/o microemulsion

Characterization technique of synthesized iron-oxide nanoparticles: The characterization of the material was performed by standard techniques. Particle size distribution and Surface area was also measured.

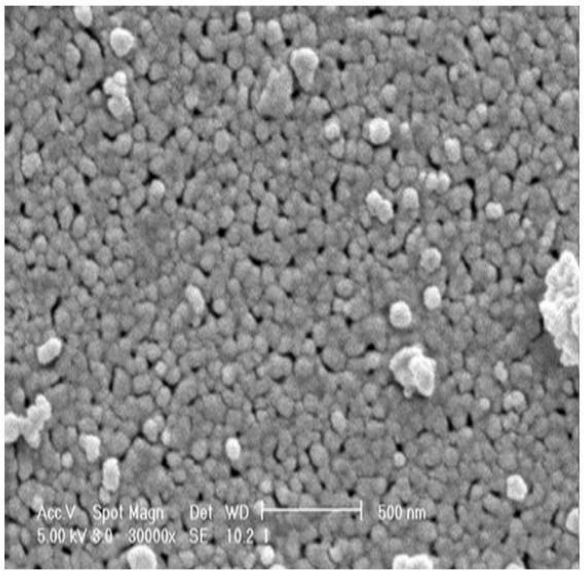
Batch Experiments

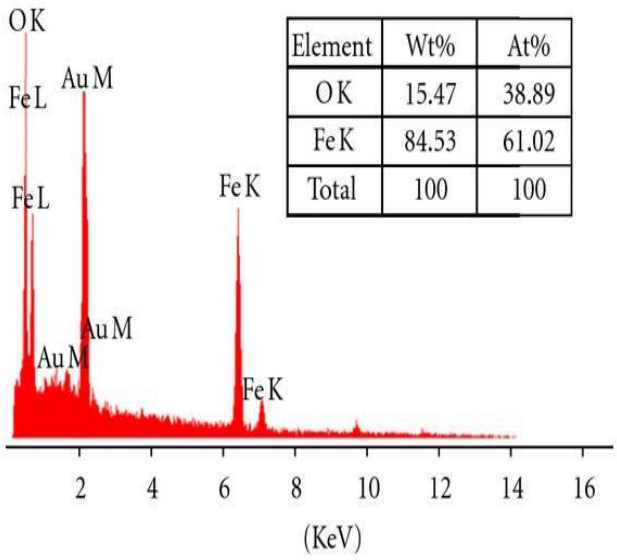
The batch experiments to study the removal of arsenic from solution were carried out by treating 50mL of As solution in100mL polyethylene bottles with desired amount of the adsorbent with varying parameters like contact time, initial concentration of fluoride, adsorbent dose, pH and temperature in order to optimize the removal process. The bottles were immersed in a shaking water bath at predetermined temperature (25, 35 and 45)$^{\circ}$C. The shaker speed was controlled at 300 rpm. After a predetermined contact time, the aqueous samples in each bottle were decanted

and centrifuged at 4500rpm for 5min, and then filtered through a 0.45µm cellulose acetate filter. The supernatant liquid was analysed for fluoride concentration before and after adsorption study was determined by ion selective electrode method [1] using Orion 720 A^+ Ion analyser. Total ionic strength adjusting buffer (TISAB-III) solution was added to both samples and standards in the ratio 1:10. TISAB-III contains 300 g sodium citrate·2H2O (FW = 294.10), 22 g of 1,2-cyclohexanediamine-*N*,*N*,*N*_,*N*_-tetraaceticacid (CDTA) and 60 g of NaCl in a volume of 1000mL (pH 5–5.5). TISAB-III solution regulates the ionic strength of samples and standard solutions, adjust the pH and also avoid interferences by polyvalent cations such as Al(III), Fe(III) and Si(IV), which are able to complex or precipitates with fluoride and reduce the free fluoride concentration in the solution. CDTA forms stable complexes with polyvalent metal cations (e.g. Al(III), Fe(III) and Si(IV)) which are more stable than metal–fluoride complexes (AlF_6^{3-},FeF_6^{3-}, etc.) in solution. The CDTA preferentially complexes with polyvalent cations present in water and/or aqueous solution (e.g. Si^{4+}, Al^{3+} and Fe^{3+}) . The electrode is selective for the fluoride ion over other common anions by several orders of magnitude.

Results and Discussion:

The iron oxide nanoparticle are synthesized and characterized by standard methods. The scanning electron microscopy (SEM) measurements were performed, in order to know the morphology of iron oxides surface. The morphology of the magnetic iron oxide nanoparticle samples was investigated by SEM. and represented in Figure-3.The SEM image and its corresponding EDX confirm the formation of the nano particle as reported in literature previously.





Element	Wt%	At%
O K	15.47	38.89
Fe K	84.53	61.02
Total	100	100

Figure-3 SEM Image and EDX spectrum of Magnetic iron oxide nanoparticle

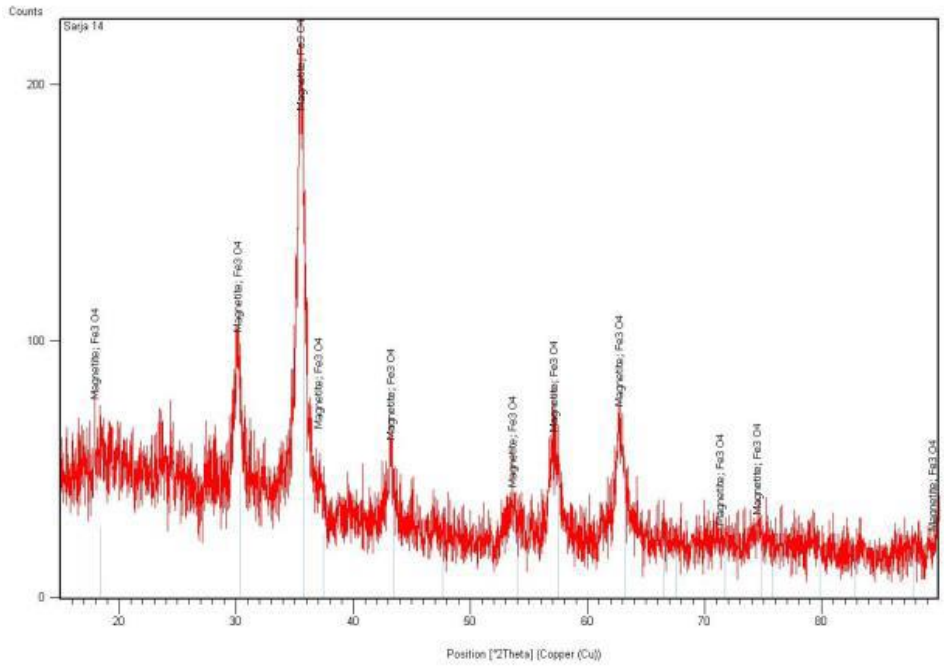


Figure-4 XRD patterns obtained for magnetite nanoparticles

The crystalline structure was verified by X-rays diffraction (XRD) at room temperature and the XRD pattern is represented in Figure-4 . Powder XRD of the material was obtained by using

PHILLIPS X'PERT X-Ray diffractometer with CuKα radiation (35kVand 30mA)at a scan rate of 1◦/min in the 2θ range from 10o to 90o and was analyzed using standard software provided with the instrument . All the detected diffraction peaks were indexed. The analyzed samples showed very broad diffraction lines, in accordance with their small particle size and high specific surface area as reported earlier in literature. The XRD pattern of the magnetic iron oxide confirms the formation of iron oxide nano particles. The other characterization process is under process. The material is then used for the removal of fluoride by batch mode.

Batch studies

(i) Effect of adsorbent dose

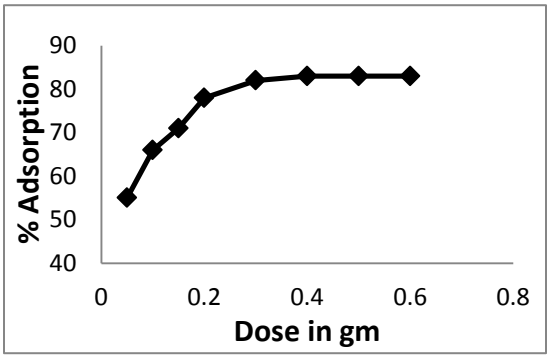


Fig. 5: Effect of adsorbent dose

Effect of adsorbent dose on fluoride removal was studied at ambient temperature (25 ± 2 °C) and contact time of 2 hrs for initial fluoride concentration of 10 mg/L. From Fig. 5, it is evident that the removal of fluoride increased from 55-83% for 1–12g/L of Fe_3O_4 nanoparticle. However it is observed that after dosage of 0.4 gm, there was no significant change in percentage removal of fluoride. It may be due to the overlapping of active sites at higher dosage. So, 4g/L was

considered as optimum dose and was used for further study. This can be attributed to the availability of surface area and hence adsorption sites.

(ii) Effect of pH

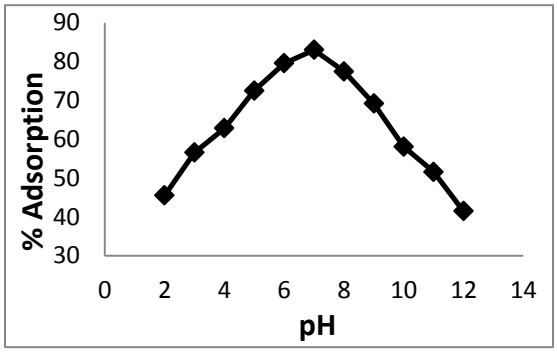
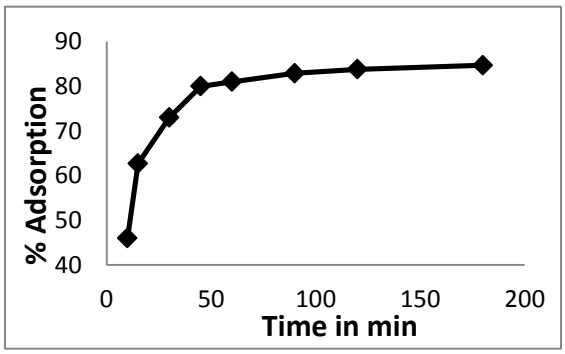


Fig. 6: Effect of pH

Adsorption of fluoride by Fe_3O_4 nanoparticle was studied in the pH range of 2–12. As shown in Fig. 6, the adsorption of fluoride increases within a pH range of 2–7 beyond which the adsorption decreases. The optimum removal of fluoride was found to be at pH range of 6.5-7.0.

(iii) Adsorption kinetics



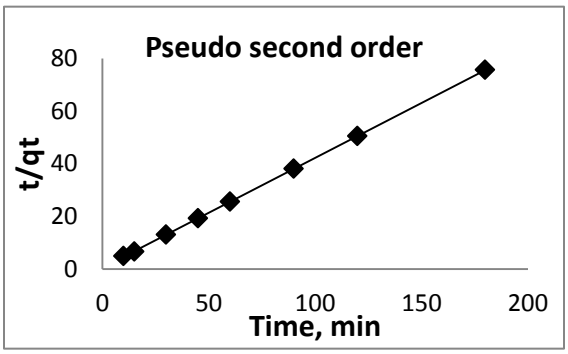


Fig. 7: Effect of contact time **Fig. 8: adsorption kinetics**

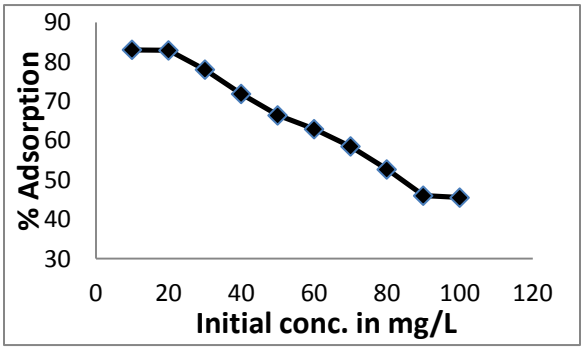
The linear form of pseudo-second order kinetic model can be expressed as

$t/q_t = 1/K_s (q_e)^2 + t/q_e$ (1)

where, K_s is the rate constant for pseudo-second order reaction (g mg^{-1} min^{-1}). q_e and q_t are the amounts of solute sorbed at equilibrium and at any time 't' (mg g^{-1}), respectively. The straight line plot of t/q_t vs t for the kinetic data gives the values for q_e and K_s from the slope and intercept, respectively.

The sorption of fluoride has been investigated with variation of time in the range of 10–180 minas shown in fig. 7. The removal amount of fluoride increases with increase in time and finally reaches a saturation level in at 120 min where almost 83.8% of fluoride removal was achieved.The pseudo second order kinetics was represented in Figure-8

(iv) Adsorption isotherm



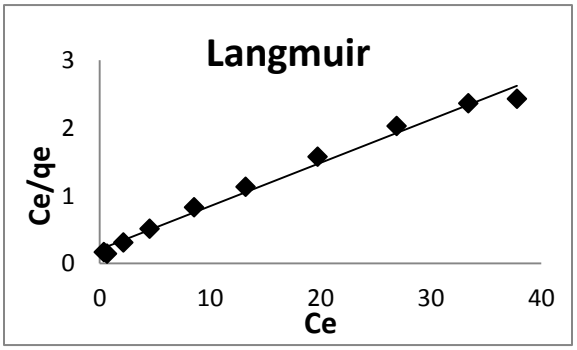


Fig. 9: Effect of initial concentration **Fig. 10: Adsorption isotherm**

The Figure-9 represents the effect of initial concentration of fluoride solution on adsorption. From the figure it is clear that the adsorption decreases with increase in the initial concentration

of the fluoride solution. However, it is clear from the above figure that, maximum removal takes place when the initial concentration is low and removal is very less at higher concentrations.

The Langmuir adsorption isotherm assumes that the adsorbed layer is one molecule in thickness and that all sites are equal resulting in equal energies and enthalpies of adsorption. The Langmuir equation can be described in the following equation:

$$q_e = (q_m K_L C_e) /(1+K_L C_e) \quad (2)$$

The linearized form of Eq. (5) can be written as:

$$1/q_e = (1/K_L q_m) (1/C_e) + 1/q_m \quad (3)$$

where, q_e is the amount of fluoride adsorbed at equilibrium (mg g^{-1}), Ce is the equilibrium concentration (mg L^{-1}), q_m is the mono-layer adsorption capacity (mg g^{-1}) and K_L is the Langmuir constant related to the free adsorption energies (L mg^{-1}). The value of q_m and K_L can be calculated, respectively, from the slope and intercept of the linear plot of $1/C_e$ vs $1/q_e$..

In order to find out the feasibility of isotherm, the essential characteristics of Langmuir isotherm can be expressed of a dimensionless constant separation factor or equilibrium parameter R_L. Thus, R_L can be expressed as:

$$R_L = 1/(1+K_L C_o) \quad (4)$$

where, C_o is the initial concentration of fluoride (mg L^{-1}). $R_L < 1$ represents favourable adsorption. The linear plot of 1/*C*e versus 1/*q*e (Fig. 10) indicates the applicability of Langmuir adsorption isotherm.In this result of fig. 10, the value of R_L for the initial fluoride concentration of 100 mg $L^{-1}$was found to be 0.0644 indicating a favourable condition of adsorption of fluoride and the value of q_m was found to be 2.953.

(v) ffect of temperature

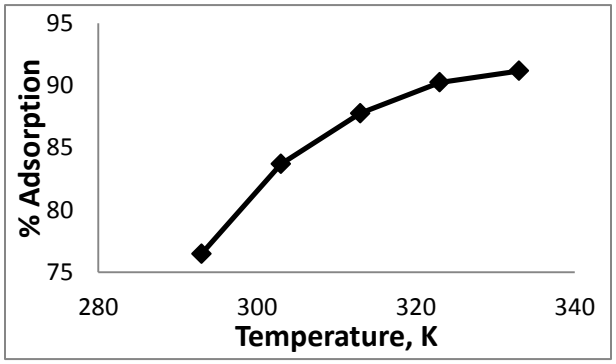


Fig. 11: Effect of temperature

The effect of temperature on the adsorption of fluoride with initial concentration 10 mg/L, examined is represented in fig. 11. as percentage removal of fluoride versus temperature. The percentage removal of fluoride with initial concentration 10 mg/L, increased from 76 – 91%, for 20°C-60°C temperature. The continuous I ncrease in percentage removal with temperature indicate that the adsorption process is endothermic in nature..

Conclusion: The magnetic iron oxide is synthesised and characterized by standard procedure. The material is used as an adsorbent for the removal of fluoride from the synthetic fluoride solution..The maximum removal of fluoride occurs at p H 7,with an adsorbent dose of 0.4gm/L, time 40 min .The adsorption follows pseudo second order kinetics. The experimental data are best fitted with the Langmuir isotherm model. Hence it is concluded that the material can be an excellent adsorbing material for fluoride for which further studies are going on.

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