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RESEARCH ARTICLE

ADSORPTION STUDIES OF MAGNETIC NANOFERRTIES IN THE REMOVAL OF HEAVY METAL ION (As^{3+}) FROM AQUEOUS MEDIA

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ABSTRACT

Arsenic and heavy-metal-contaminated environments are a major concern due to their negative impacts on exposed people and ecosystems. Nanosized spinel ferrites Samarium (Sm^{3+}) doping Nickel-Magnesium nano spinel ferrite [$Sm_{0.2}$, $Ni_{0.2}$, $Mg_{0.2}$, Fe_2O_4] (SNM) have been prepared by sol-gel auto-combustion method. The spinel ferrites have been applied for As^{3+} ion adsorption using batch technique. The effects of pH, contents of loaded magnetic matter nanoparticles, adsorbent dose, contact time, and temperature on adsorption capacity of the magnetic beads were investigated. All the results suggested that the mentioned nanoparticles could be excellent adsorbents for As(III) contaminated water treatment. Batch experiments were revealed that As removal was up to >85% using SNM as adsorbent material. Adsorption isotherm studies revealed that Langmuir isotherm was followed with a better correlation than the Freundlich isotherm. The kinetic studies indicated that adsorption of all selected metal ion could be well described by the pseudo second-order kinetic model. These values show that the adsorption is endothermic and spontaneous in nature. Finally it was concluded that the prepared adsorbent combines the advantages of magnetic nanoparticles with magnetic separability and high affinity toward arsenic metal ions, which provides distinctive merits including easy preparation, high adsorption capacity, and easy isolation from sample solutions by the application of an external magnetic field. The adsorption behaviors of arsenic from an aqueous medium, using SNM magnetite nanoparticles were studied by using equilibrium batch techniques.

Keywords: SNM, Adsorption, Isotherm study, Kinetics

1.0 Introduction

Arsenic is a well-known toxic metal and is present mainly as oxyanion compounds in groundwater[1]. The World Health Organizationís (WHO's) current provisional guideline for arsenic in drinking water is 10 µg/L, but all developing countries affected with contaminated groundwater are still struggling to keep up with the previous WHO guideline value of 50 µg/L[2]. Chronic exposure to arsenic >50 µg/L in drinking water can result in serious health problems. Symptoms of chronic exposure to groundwater contaminated with arsenic at concentrations significantly >50 µg/L include skin, cardiovascular, renal, hematological and respiratory disorders (Smedley P.L et al., 2002). An estimated 300,000 people in West Bengal alone suffer from arsenic-induced skin lesions. Serious illnesses related to arsenic such as melanosis, keratosis, cancer, and gangrene have been reported in West Bengal and Bangladesh[3]. Widespread arsenic contamination of groundwater has led to a massive epidemic of arsenic poisoning in Bangladesh and neighbouring countries. It is estimated that approximately 57 million people are drinking groundwater with arsenic concentrations elevated above the World Health Organization’s standard of 10 parts per billion. Nanometer-sized materials have attracted substantial interest in the scientific community because of their special properties. For many developing countries, groundwater is the main source for water consumption in rural and urban areas. The occurrence of arsenic in groundwater is an environmental problem due to its high toxicity. Literature review of arsenic removal technologies and procedures indicates that iron filings, ferric salts, granular ferric hydroxide, alumina manganese oxide, etc., tailings are potentially adsorbents that can remove arsenic after simple mixing in a relatively short time. However, all these technologies suffer from significant shortcomings. Synthetic sorbents are highly selective and effective and do not pose a significant waste disposal concern because they are generally non-hazardous[4]. Magnetic separation technique, using magnetic polymeric particles, is a quick and easy method for sensitive and reliable capture of inorganic or organic solutions. The magnetic sorbents behave similar to or even better than various commercial adsorbents.[5] Although the removal of arsenic by different technologies has been proven, adsorption is one of the best alternatives due to its simplicity and low cost. In particular, nanoadsorbents incorporating magnetic properties are promising separation agents because of their advantageous and efficient potential recovery in a magnetic field, characteristic that is very attractive and of utmost relevance in the development of low cost technologies to provide drinking water in developing countries[6].

2.0 Experimental

2.1 Material and Method

All chemicals and solvents were AR grade or better purchased from Merck Co.Pvt Ltd and Sd. fine chemical used without any further purification. The stoichiometric amounts of metal nitrates (Ni, Mg, and Sm) Citric acid - ($C_6H_8O_7.H_2O$) used as starting materials for the synthesis.

2.2 Synthesis of nanoparticles

Metal nitrates in required proportions were dissolved in a minimum quantity of distilled water and mixed together. Aqueous solution of Citric acid was then added to the mixed metal nitrate solution (with and without Samarium nitrate). Ammonia solution was then added with constant stirring by maintaining the neutral pH (7.0). The solutions were heated at 90ºC under continuously stirring to remove the excess of the solvent. By raising the temperature up to 200°C lead the ignition of gel. The dried gel burnt completely in a self-propagating combustion manner to form powder like substance. The burnt powder was ground in Agate Mortar and Pestle to get a fine Ferrite powder. Finally the burnt powder was calcined in air at 700°C temperature for 2 hours and cooled to room temperature.

2.3 Standard Arsenic Solution. Analytical grade As(III) oxide (As_2O_3), was used to prepare stock solutions of 1000 mg/L As(III) stock solution. As_2O_3 chemicals were procured from Loba Chemical Industries, India. The Secondary As(III) ion standard ranging from 1 to 100 mg/L were prepared from the stock solution for the generation of the calibration curves for As detection. The heavy-metal concentrations were quantitatively measured with the help of Elico-made AAS in accordance with the standard method.

2.4 Batch Adsorption Process

Batch experiments were carried out to understand the adsorption behavior and study the kinetics of heavy metal adsorption. In separate experiments, 100 mg/L (0.01 wt %) SNM as adsorbent material was added to the heavy-metal solutions of varying concentrations ranging from 10 to 100 mg/L made up from stock solution using 0.01 M $NaNO_3$ solution as background electrolyte to keep the ionic strength optimum for adsorption.[7] McBridge[8] suggested that the dominant surface interaction between adsorbate ion forming outer sphere complexation with an adsorbent surface shows decreasing adsorption with increasing ionic strength of the solution.[9] For understanding the adsorption behavior of the nanoparticles, heavy-metal solutions of varying concentration were agitated on Remi shaker for 30 minutes. The adsorption behavior of the nanoparticles was investigated at different pH values of the heavy-metal solution under study. The solution pH was adjusted by using 1 M NaOH and 1 M HNO_3 as required. For kinetic studies, the pH was fixed at a value corresponding to maximum adsorption. The initial concentration of the heavy metal was fixed at 30 mg/L and adsorption time was varied from 5 to 90 min. The adsorption isotherm was tested to validate the heavy-metal uptake behavior of the nanoparticles. All samples were analyzed after removing the SNM from the sample by using a small magnet as well as filtration through Whatman filter paper (41 Size). Adsorption behavior was studied at room temperature

3. RESULTS & DISCUSSION

In general, the sol-gel process involves several successive stages: (a) formation of sol which represents a colloidal suspension containing small particles with a diameter less than 1000 nm dispersed in a continuous liquid medium, (b) the gelation of the sol to give a three-dimensional M–O–M/M–OH–M network whose pores are filled with solvent molecules (wet gel), (c) the ageing of the resulting wet gel process known as syneresis, (d) the elimination of the solvent from the gel's pore (drying). The aim of the present work is to prepare modified nanoparticles of magnetite spinel ferrites SNM. The magnetic nanocomposite was used for determination and adsorption capacity of arsenic ion from aqueous medium under batch equilibrium conditions. The effect of various experimental parameters such as aqueous phase pH, adsorbent dose, time and Concentration and the magnetic property of the SNM, respectively were tested.

3.1 Effect of pH

The effect of pH on removal of arsenic is on to SNM shown in Figure 3.1. The study was done in the pH range of 1.0 to 11. It was found that the adsorption of arsenic ion gradually increases as the initial pH of the solution is raised from 3 to 7. The maximum removal of arsenic was found to be 88.94%, at pH 7. Hence, pH of the arsenic solution was maintained at 7 for further study. This agrees with the other results obtained on iron oxide coated on cement (IOCC)[10], carbon based adsorbents[11], and zero valent iron[12]. At pH more than 7, the removal process is very low. This is due to high OH– ion concentration, which reverses the process of removal, and hence the process of conversion of adsorbent into its OH– form plays an important role leaving behind arsenic in the aqueous solution. This is due to the effect of precipitation of Arsenic.

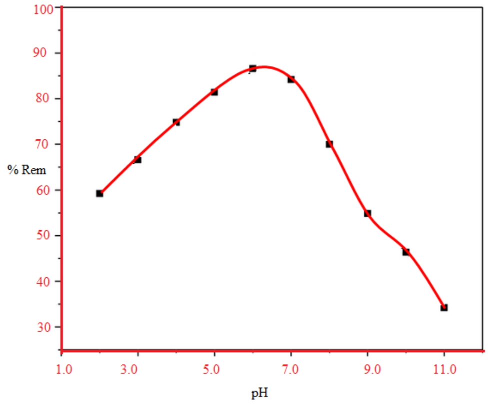

Figure 3.1: Effect of pH on adsorption of arsenic ion removal onto SNM

3.2 Effect of Adsorbent Dose: The effect of adsorbent dose on the removal of As^{3+} ion was studied at room temperature (30±1°C) and contact time of 30 min for initial As^{3+} ion concentration of 10 mg/L. The results are presented in Figure 3.2. It is evident from the figure that the removal of As^{3+} ion increased from 99.89-99.90 % for 4 g of SNM material in 100 ml of arsenic content solution of initial arsenic (III) concentration of 10mg/L.

However it is observed that after dosage of 3g, there was no significant change in percentage of removal of As^{3+} ion. It may be due to the overlapping of active sites at higher dosage. So, there wasn't any appreciable increase in the effective surface area resulting due to the conglomeration of exchanger particles[13] (T. Helledy et.al., 2000). So, 3 g/L was considered as optimum dose and was used for further study.

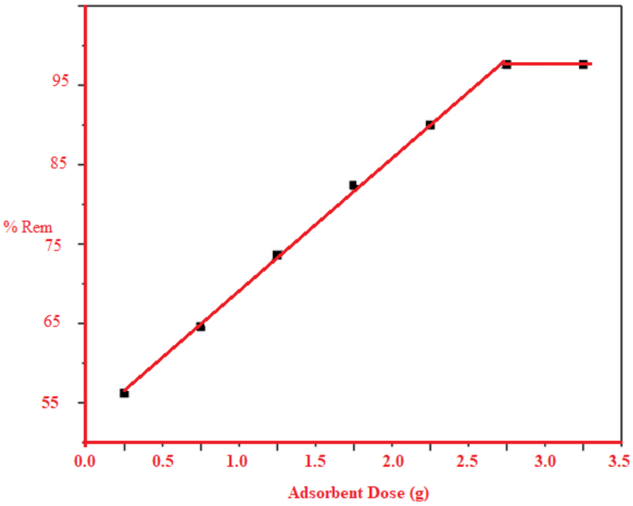

Figure 3.2: Effect of adsorbent dose on adsorption of arsenic ion removal onto SNM

3.3 Effect of initial Arsenic Concentration

The adsorption of As^{3+} ion onto SNM Adsorbent was studied by varying initial As (III) concentration using optimum adsorbent dose (3 g/L) at room temperature and contact time of 30 minutes. The results are represented in graphical form as percentage removal versus initial As^{3+} ion concentration. The initial arsenic concentration was increased from 10 mg/L to 100 mg/L and the corresponding removal gradually increases from 90.00 % to 98.7 %. However it is cleared from the figure that, there wasn’t any appreciable decrease in percentage removal with increase in concentration of As^{3+} ion sample. This may because of the fact that at higher adsorbate concentration, the free sites available to occur saturation, resulting in adsorption towards higher extent.

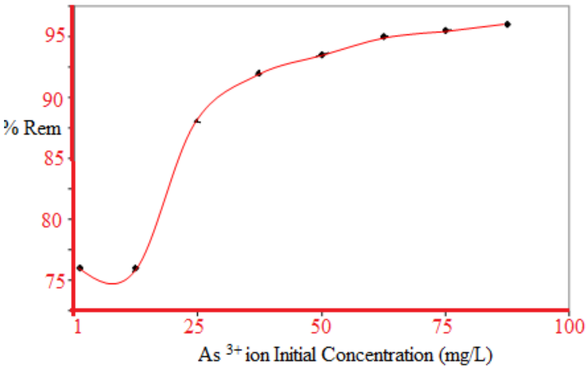

Figure 3.3: Effect of initial Arsenic Concentration

3.3.1 Adsorption isotherms: The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. Langmuir and Freundlich isotherm equations are the most widely used models to describe the experimental data of adsorption isotherms. As(III) ion adsorption isotherms obtained for SNM adsorbent was shown in figure 3.4 & 3.5. These isotherms represent the adsorption behavior of As(III) on the different adsorbents as a function of increasing aqueous As(III) ion concentration for a contact time of 30 minutes. All the isotherms show that the adsorption capacity increases with increasing equilibrium concentration of As(III) ion, but the increasing slope of SNM adsorbent is 19.28 The results of As(III) adsorption on SNM was analysed by using the

Langmuir model to evaluate parameters associated to the adsorption behavior. The linear form of Langmuir equation at a given temperature is represented by:

$$qe = qm \cdot b \cdot Ce/(1 + b \cdot Ce) \ldots\ldots\ldots.1$$

Where ce is the aqueous phase ion equilibrium concentration (mg/L), qe is the amount of As(III) sorbet onto 1 g of the considered adsorbent (mg/g), b is the adsorption constant (L/mg) related to the energy of adsorption and qm is the maximum adsorption capacity (mg/g).

Equation (1) can be rearranged to obtain:

$$Ce/qe = 1/(b \cdot qm) + ce/qm \ldots\ldots.2$$

Experimental isotherm data acquired were correlated with the linear form of Langmuir model. The isotherm parameters related to the model were listed in Table 1. It could be seen that both qm and b remain the higher for As(III) adsorption onto SNM sample. High value of b was reflected in the steep initial slope of an adsorption isotherm, indicating desirable high affinity. Therefore, SNM adsorbent performed well in As(III) adsorption. The Freundlich isotherm model was also used to analyse the result of As(III) adsorption on different adsorbents (Figure 3.4). The Freundlich model can be expressed by the following equation:

$$q_e = k_f \cdot Ce^{1/n}$$

Where k_f and n are constants related to the adsorption capacity and affinity, respectively. The equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$Log\ (qe) = Log\ (kf) + \left(\frac{1}{n}\right) Log\ (ce)$$

Experimental isotherm data acquired on different adsorbents were fit with the linear form of Freundlich model and the isotherm parameters related to the model were listed in Table 1. The data showed that the kf constant is higher for iron oxide/activated carbon than that for activated carbon, 1/n value for SNM composite is 0.195, these imply more favourable adsorption of As (III) on SNM.

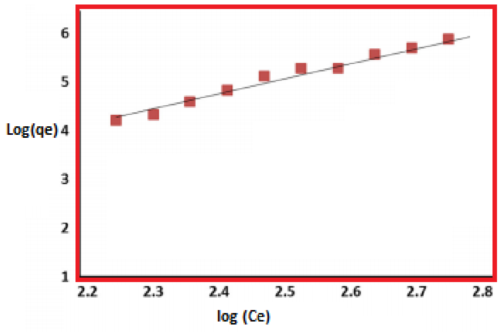

Figure: 3.4: Freundlich Isotherm

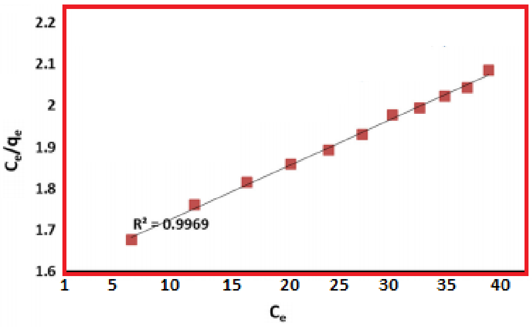

Figure 3.5 Langmuir Isotherm

3.4 Effect of contact time

Contact time is one of the effective factors in batch adsorption process. The effect of contact time on As(V) adsorption efficiency was shown in Figure 3.6. As it is shown, the removal efficiency of As (III) onto the SNM adsorbent significantly increase during the initial adsorption stage (0–30 min) and then continue to increase at a relatively slow speed with contact time until a state of equilibrium is attained after 50 min. There was no significant change in As(III) removal rates after 60 minutes. Based on these results, 30-40 minutes was taken as the time in adsorption experiments. Generally the removal rate of adsorbate is rapid initially, but it gradually decreases with time until it reaches equilibrium. This phenomenon can be attributed to the fact that a large number of vacant surface sites are available for adsorption at the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Similar findings were reported by other researchers[14].

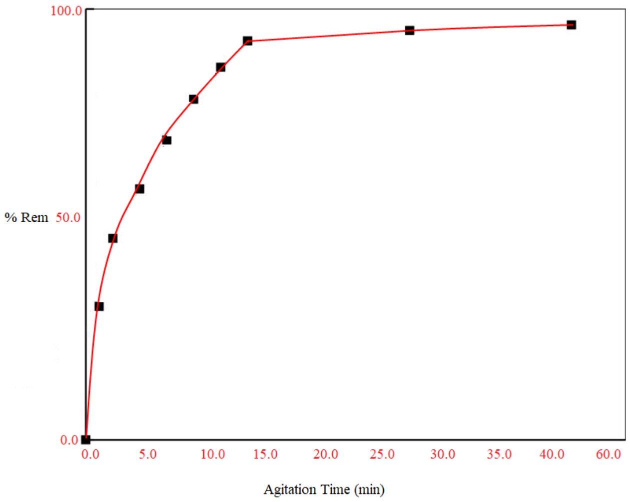

Figure 3.6: Effect of contact time on the adsorption of As(III).

Table 1: The parameters of Langmuir and Freundlich equation

Adsorbent	**Langmuir equation**			**Freundlich equation**		
	qm(mg/g)	**B (L/mg)**	**R^2**	**1/n**	**K_f**	**R^2**
SNM	19.289	0.196	0.996	0.195	7.901	0.9578

3.5 KINETIC STUDY

The kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of sorption. In the present study, the kinetics of As (III) ion removal was carried out to understand the behavior of prepared SNM adsorbent.

3.5.1 The pseudo first-order equation

The pseudo first-order equation proposed by Lagergren[32] is given by

$$\frac{dq_t}{d_t} = k_1(q_e - q_t) \ldots\ldots\ldots\ldots (3.5.1)$$

Where, *qe* and *qt* are the adsorption capacity at equilibrium and at time *t*, respectively (mg/g), k_1 is the rate constant of pseudo first-order adsorption (l·min^{-1}). After integration and applying boundary conditions *t* = 0 to *t* = *t* and *qt*= 0 to *qt*=*qt*, the integrated form of Eq. (3.15) becomes:

$$\ln\left(\frac{q_e}{q_e - q_t}\right) = k_1\, t \ldots\ldots\ldots\ldots\ldots (3.5.2)$$

Eq. (3.5.2) can be rearranged to obtain a linear form

$$Log\ (q_e\text{-}q_t)= log\ (q_e)\text{-}k_1\ t \ldots\ldots\ldots\ldots\ldots\ldots. (3.5.3)$$

The values of *log (qe - qt)* were linearly correlated with *t*. The plot of *log (qe - qt)* vs. *t* (fig 3.7)should give a linear relationship from which $k_1$and *qe* can be determined from the slope and intercept of the plot, respectively.

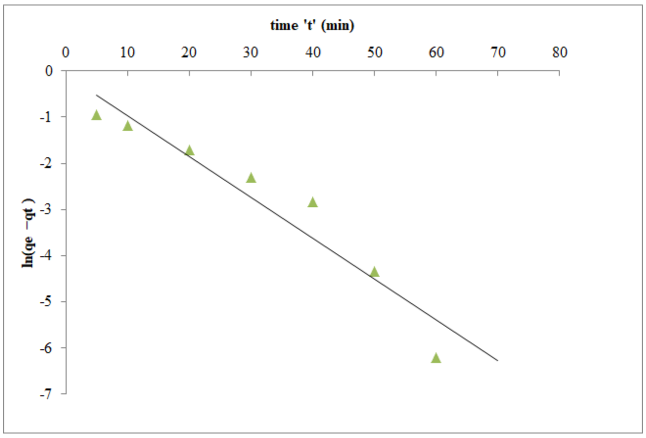

Figure 3.7: Pseudo-First order Kinetics for the As (III) ion adsorption onto SNM

3.5.2 Pseudo-second-order kinetic model

The pseudo second-order adsorption kinetic rate equation is expressed as[35-36]

$$\frac{t}{qt} = \frac{1}{K_2 {q^2}_e} + \frac{1}{qe}(t) \ldots\ldots\ldots\ldots\ldots..(3.5.4)$$

The plot of (*t/qt*) and *t* of Eq. (3.5.4) should give a linear relationship from which *qe (1/slope)* and k_2 *(slope*^{2}*/Intercept)* can be determined from the slope and intercept of the plot, respectively. Available studies have shown that the pseudo-second order rate equation is a reasonably good fit of data over the entire fractional approach to equilibrium and therefore has been employed extensively in the study of adsorption kinetics. However, it is not uncommon to observe multi linearity on the *t/qe* Vs *t* plot (Fig 3.8). The trend is usually such that the rate constant decreases with time or more specifically decreases with increasing solid phase concentration.

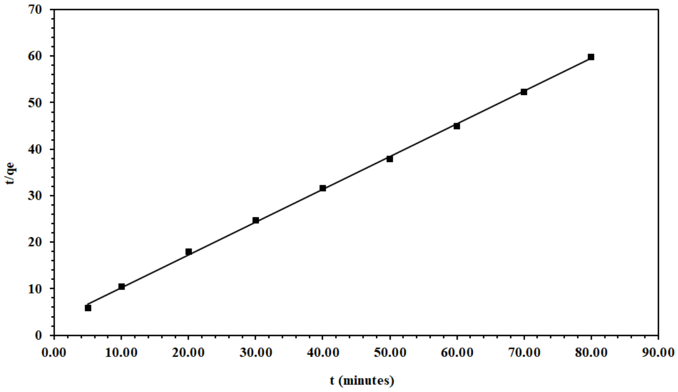

Figure 3.8: Pseudo-Second order Kinetics for the As (III) ion adsorption onto SNM

The fitting of the kinetic data demonstrate that the dynamics of sorption could be better described by pseudo second-order model indicating a chemisorptive rate-limiting for all the three adsorbent SNM

4.0 Magnetic properties

The magnetic parameters of prepared nano ferrite samples were calculated by using a vibrating sample magnetometer (VSM) in the range 5000 Oe, where the samples displayed the magnetic behaviour. The hysteresis loops (figure 4.1) were plotted from the VSM measurements, from which the saturation magnetisation values for the different compositions Sm_x, $Ni_{0.2}$, $Mg_{0.2}$, Fe_2O_4 (x=0.0, 0.02, & 0.04) were calculated and represented graphically in Figure 4.1 and tabulated in table 2. The variation of saturation magnetisation with composition is as shown the figure 4.1 and figure 4.2, it was evident from the hysteresis loops that the sample does not saturate completely for values (x= 0.0, 0.02 0.04). From the result it is clear that the saturation magnetization decreases with the substitution of Sm^{3+}. This decrease can be explained based on the site occupancy of the cations and also the modification in the exchange effects caused by substituting Sm^{3+}. The Fe^{3+} ions occupying the 'B' sites in the inverse spinal lattice are the main contributors of the magnetic properties. Sm^{3+} paramagnetic in nature due to no unpaired electrons. There is a significant decrease in the coercivity with the substitution of Sm^{3+}. This theory states that the factors such as micro strain, magneto crystalline anisotropy, magnetic particle morphology, magnetic domain size and size distribution influence the coercivity[11].

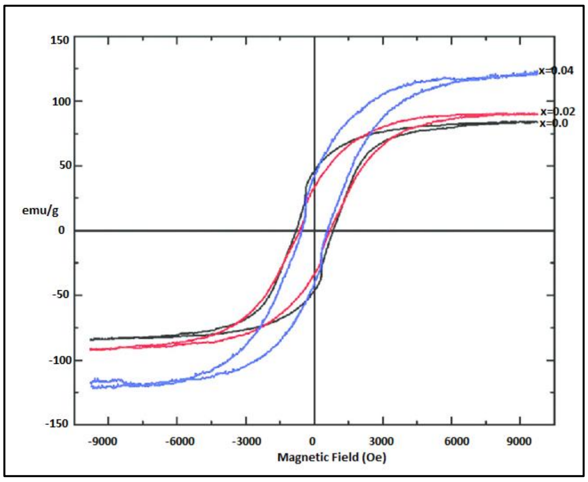

Figure 4.1: Hysteresis loops of Ni-Mg ferrite for various Sm^{3+} concentrations

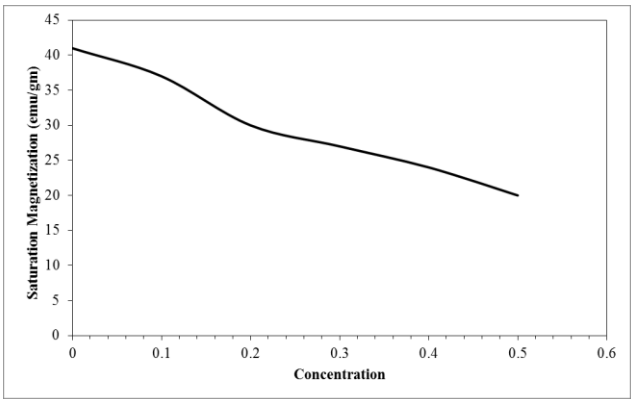

Figure 4.2: Plot of Magnetization Vs Concentration

Table 2: Magnetic Properties of Spinel Ferrites

Concentration of Sm^{3+} ion	Magnetization (emu/g)	Coercivity (Oe)	Retentivity (emu)
0.0	21.8471	14025.21	17.264
0.02	20.6487	17245.34	16.257
0.04	18.9842	16824.57	16.128

5.0 Conclusion

This work aimed at the development of the methodology for analyzing the performance of an adsorption process based on the use of functionalized magnetic nanomaterials as adsorbents, to carry out the selective separation of the target compound, arsenic, from aqueous media, which simulates the typical composition of polluted groundwater. A magnetic composite adsorbent was successfully prepared with SNM as Adsorbent materials for the removal of As(III) from solution. The adsorption properties of the SNM adsorbent for As(III) depend on contact time, initial solution pH, adsorbent dosage etc.,. The adsorption kinetic data of As(III) can be illustrated very well by the pseudo-second-order rate equation. The equilibrium data obtained from this study was well presented by Langmuir and Freundlich models. Magnetic parameters decrease with increasing Sm^{3+} substitution. The steady increase in the Sm^{3+} concentration carried about a decrease in the crystallite size tailed by a decrease in the saturation magnetisation

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