Selenium Removal from Water Using Bimetallic Nanoadsorbent

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***Abstract*: Selenium in wastewater is of particular concern due to increasing concentration, high mobility in water and toxicity to organisms. Selenium ions are toxic at concentration above 40µg/L. This study was carried out to determine the removal efficiency of selenium using iron and manganese based bimetallic nano-adsorbent. In this study bimetallic nano-adsorbent was synthesized by using chemical reduction method, nano particles were characterized by using Energy Dispersive X-ray Spectroscopy (EDX), Scanning Electron Microscopy (SEM), Brunauer, Emmett and Teller (BET), Zeta particle size and then it applied to remove selenium ions in aqueous system. The selenium removal efficiency was optimized by varying the parameters such as contact time, Se concentration, dosage of adsorbent and pH of solution. The pH effect was investigated between 6-9. Results confirmed that alkaline (8.5) pH enhanced the selenium adsorption capacity towards nano-particles. The optimized dosage of adsorbent was 25mg and the optimized contact time was 60 minutes. The reusability of nanoparticles was also studied. Both Langmuir and Freundlich adsorption isotherm models were also calculated. In this study results show that overall adsorption capacity of bimetallic nano-adsorbent towards the removal percentage of selenium is 95% under optimized conditions.**

***Keywords*: Adsorption, Bimetallic, Iron, Manganese, Selenium, Water Treatment.**

I. INTRODUCTION

Selenium is a chemical element with symbol Se and atomic number 34 that has chemical and physical properties same as in between those metals and non-metals. Selenium exists in different oxidation states, most dominant oxidation state is Selenate (Se^{6+}) because of its rapid solubility in soil other is Selenite (Se^{4+}) that has greater affinity for adsorption on soil particles surfaces and has low solubility [1], [2]. The presence of selenium in aquatic environment is caused due to naturally as well as synthetically. There are several natural sources which cause the presence of selenium in water such as weathering of soil and rock volcanic eruption, chemically inter conversion in coal mines. Selenium found in water due to men made activities which consist on coal combustion industry, agricultural activities; mining, oil and gas refine process, pesticide production, glass and cement industries. One of the major sources of Selenium in aquatic environment is the coal combustion process, during power generation solid waste and flue gases are released into the environment which contributes high concentration of selenium in water in the form of SeO_2 and SeO gases [3],[4]. It has been estimated that anthropogenic activities are responsible globally for releasing 76,000-88,000 tons of selenium per year into the soil and water which is then transferred to animal organisms, plants and life cycle which results in a serious environmental and health effects [5], . Once it reached in aqueous environment it attain rapid toxic level which affects fishes and wildlife due to bioaccumulation of food chain results in dietary exposure. Even the slight increase in concentration can cause total reproduction failure in fishes with a very limited range of few µg/L [6]. Recent studies and case reports have shown that there are several adverse health effects when selenium compound's exposure to human goes for a long term. Most early toxic effect of selenium may cause on endocrine function, especially on the synthesis of thyroid hormones following dietary exposure of around 300µg Se/d, insulin growth factor and growth factor's metabolism can also be effected [7], [8]. There are also other adverse health effects of Selenium if intake in an excessive level are skin and scalp bruise, hairs and nails irregularity including losses [9].

On the basis of USEPA the risk assessment of the selenium can be categorized to its exposure level:

1) Short term exposure: EPA found selenium has adversely health effect on humans when they are exposed above the MCL (maximum contaminant level) even when they are exposed for relatively less time period, these effects may include hair and fingernail changes, peripheral nervous system damage; irritation and tiredness [10].

2) Long-term: Selenium has the potential to cause the following effects from a lifetime exposure at levels above the MCL: hair and fingernail loss; liver tissue; damage to kidney, and the nervous and circulatory systems [10].

Many technologies have been introduced for the selenium removal from water including bacterial reduction, chemical reduction, and reverse osmosis [11], [12]. However these technologies have some limitation in their own aspects so new alternative technologies for the adsorption of selenium are being discovered [13]. The adsorption of selenium towards iron oxide impregnated carbon nanoparticles has shown efficient results [14]. Other material like Fe_3O_4 Chitosan nanocomposite hollow fiber, organic ligand of benzoic acid, Hematite modified magnetic nanoparticles, and Bimetallic Oxide Nanohybrid also have high selenium removal efficiency in water [15], [16], [17]. These methods have some drawback in using the adsorbent technology due to preferential adsorption of either of the Selenite or Selenate towards that particular adsorbent, there are very few of them which removes both of the selenium anion in the water [18]. However there are many other conventional water treatment for Selenium removal technologies are also available but each of them have some disadvantages such as high residual selenium concentration and large volumes of sludge containing selenium. [19].

Nanotechnology is a wide discipline field which has great potential in the field of pollution control and water treatment processes. In the other hand application of nanoparticles are also favorable due to low cost of preparation and environmental friendly nature due to this nanoparticles are being focused for many recent studies [20], [21], [22].

This study was carried out to evaluate the adsorption performance of Fe-Mn based bimetallic nanoadsorbent for removal of selenium in water. The objectives of this study were to:

- To synthesize and characterize Iron and Manganese based bimetallic nano-adsorbent.
- To evaluate selenium removal using bimetallic nano-adsorbent and compare the removal efficiency of selenium with different literature studies.

II. MATERIALS & METHODS

A. Materials

Selenium (IV) Oxide (SeO2) (Mw= 110.96g), Iron (II) Chloride Hexahydrate, Manganese Chloride, Sodium Tetrahydridoborate 97+%, Hydrochloric Acid and Sodium Hydroxide was purchased from Sigma Aldrich (USA). All the chemicals used were of analytical grade.

B. Preparation of (Fe-Mn) Bimetallic Nanoparticles

Nanoadsorbent was synthesized by the chemical reduction method by making two separate solution i.e iron and manganese solution and the sodium tetraborate solution. Solution of salts was prepared by using Iron Chloride and Manganese Chloride with equal ratio, which was dissolved in 100ml of distilled water. And solution of sodium tetraborate was prepared by adding 200mg of sodium tetraborate in 50 ml of solution. Solution of salts was placed on the magnetic stirrer for proper mixing while solution of sodium tetraborate was added drop by drop into the solution of salt for the preparation of nano particles. Addition of sodium tetraborate was continued until the solution became dark brownish color which indicates the formation of nano particles. Then solution was filtered by using filter paper and the particles were collected separately. Collected particles were dried in the oven at 100ºC for 24 hours.

C. Batch Adsorption Studies

Different Selenium Concentration (0.1ppm, 0.5ppm, 1ppm, 5ppm, 8ppm, 10ppm) solutions of working volume of 50ml were prepared in round bottom flask with weighted amount of 25mg of adsorbent (Bimetallic NPs) and stirred at 100 rpm for 60 minutes on Shaker. NaOH and HCl were used to adjust the pH of the solution. Adsorption concentration, Adsorbent dose, shaking time and effect of pH were investigated and the residual selenium concentrations were analyzed on hydride generation atomic adsorption spectrophotometer (AAS).

Adsorption Capacity Calculation

The percent adsorption was calculated by using the following equation;

$$Q_e = \frac{(C_o - C_e)}{m} \times V$$

Where:
Qe=Removal Capacity (mg/g),
Co= Initial concentration (mg/l),
Ce=Final concentration (mg/l),
V= Volume of the solution (l),
m= Mass of nano particles (g).

III. RESULTS AND DISCUSSION

A. Characterization of Bimetallic Nanoparticles

Fig.1 (a) indicates the SEM images synthesized bimetallic nanoparticles at magnification of 5µm. Elemental analysis of Fe-Mn bimetallic nanoparticles were examined by using EDX analysis. Elemental analysis of the particles was carried out to confirm the adsorption of selenium on the particles after being used. Typical EDX spectrum of bimetallic nanoparticles is shown in fig.1 (b) Strong peak in the EDX spectra indicates the presence of Selenium at 1.5 kilo electron volt (keV). The surface area of nanoparticles which was measure by N_2 adsorption at 77 K by using Brunauer-Emmett-Teller (BET) analyzer (Quantachrome ASiQwin) was found to be 59.345m^2/g as shown in Fig.2 (a). Fig.2 (b) shows the average size of nanoparticles that is 398 nm measured by particle size analyzer (Malvern Instruments Ltd) which provides better adsorption of selenium on the surface of nanoparticles.

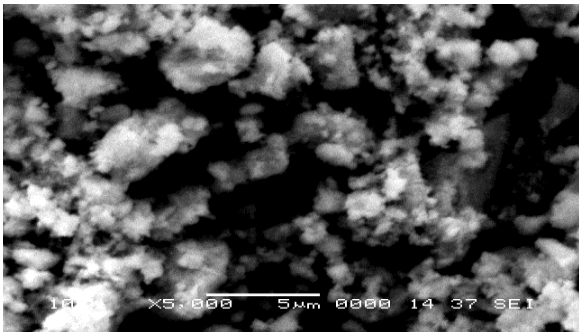
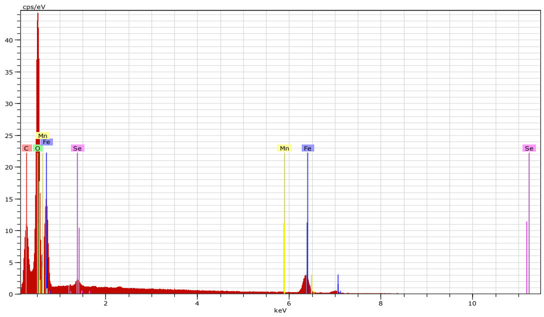


Fig. 1: (a) SEM image



(b) EDX Spectrum

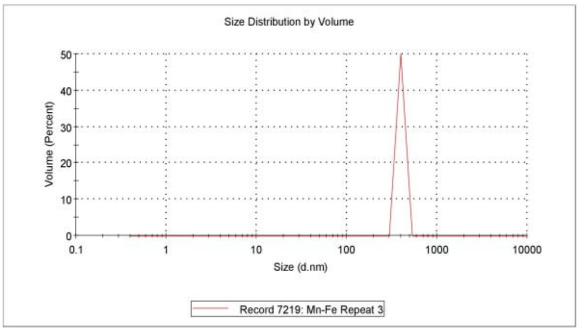
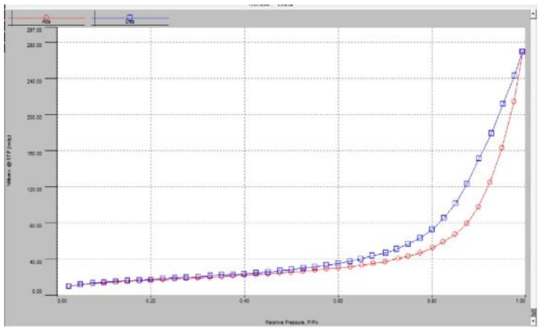


Fig.2 (a) Zetaparticle Size



(b) BET analysis of nanoparticles

B. Adsorption Isotherms

The isotherm models of Langmuir and Freundlich were used to fit the experimental adsorption equilibrium data of selenium on Fe-Mn Bimetallic nanoadsorbent. These adsorption models are represented as follows:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b} \cdot \frac{1}{C_e} \qquad \textit{(Langmuir Isotherm)}$$

$$q_e = K_f C^{1/n} \qquad \textit{(Freundlich Isotherm)}$$

Where Ce (mg/l) is the equilibrium concentration, qe (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbate, and q_m and b are the Langmuir constants related to adsorption capacity and rate of adsorption, respectively. K_f and 1/n are the Freundlich constants related to the adsorption capacity and adsorption intensity respectively. The Langmuir and Freundlich adsorption isotherms for the selenium adsorption have been shown in the fig. 3 and fig. 4 respectively. Both the graphs 1/qe vs 1/ce and lnqe vs lnce showed straight line and the empirical constant can be determined from the kinetic data.

In the present work Freundlich model gives better values of adsorption as compare to the Langmuir model because R^2 value is near to the 1 in the Freundlich model.

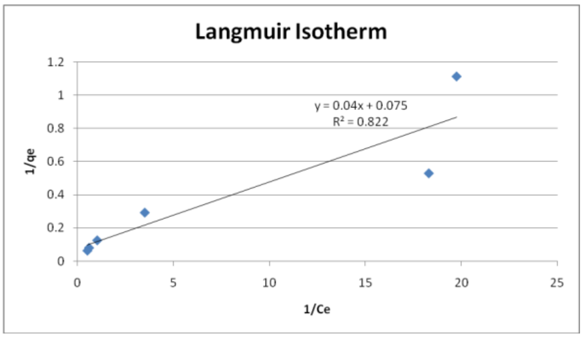


Fig.3 Langmuir isotherm for selenium adsorption

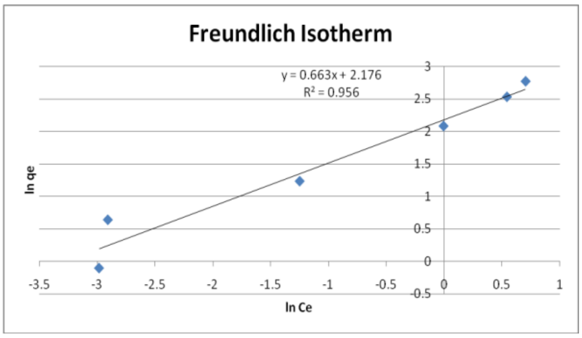


Fig.4 Freundlich isotherm for selenium adsorption

Application of Freundlich models shows a linear relationship (R^2=0.956) as seen in fig. 4 exists between qe vs ce when plotted on a log-log scale. The value of 1/n of the Freundlich model comes in between the range of 0 to 1 indicates favorable adsorption [23]. However 1/n value of 0.633 represents good adsorption characteristics. In addition Freundlich adsorption applicability reveals that adsorption of selenium took place heterogeneously due to diversity of adsorption sites provided by bimetallic nanoparticles. The isotherm constants for the parameters of these models are shown in Table 1.

Table 1: Isotherm constants

S#	Isotherm Model	Isotherm Constant		R^2
1	Langmuir Isotherm	adsorption capacity q_m (mg/g) 25	rate of adsorption b (lit/mg 0.533	0.822
2	Freundlich Isotherm	adsorption capacity k_f (mg/g) 8.810	Adsorption intensity 1/n 0.633	0.956

C. Selenium Removal by Fe-Mn bimetallic nanoparticles

a) Effect of pH

The pH of solution is a significant parameter in driving process of adsorption. In this study, the effect of pH on the selenium removal was experimented. To investigate the pH value on the performance of removal efficiency of selenium by bimetallic nanoadsorbent, samples were prepared at various pH values i.e. 6.5, 7, 7.5, 8, 8.5, 9 with an initial concentration of 10ppm, adsorbent dosage of 0.5g/l, at 60 minutes of adsorption time. Results showed that removal efficiency of selenium towards bimetallic nanoadsorbent was higher (78.69%) at pH 8.5 that may be due to anionic SeO_2 and positively charged adsorbent surface because surface charges of bimetallic nanoadsorbent is positive at pH 8.5 and negative at pH ≥ 9. It shows that alkaline pH level increases the selenium ion adsorption efficiency; similar effect was also observed in the study of [18]. Further increase in pH decreased the selenium adsorption efficiency towards bimetallic nanoadsorbent due to the repulsion of particles and selenium ions as shown in fig. 3.

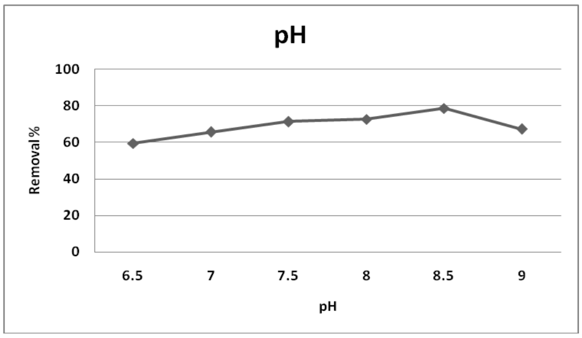


Fig. 2 Effect of pH

b) Effect of Initial concentration of selenium

Effect of Adsorbate concentration was analyzed by adding different amount of selenium concentration ranging from 0.1-10mg/l with 0.5g/l of adsorbent dose at pH 8.5 were agitated for 60 minutes at horizontal rotary shaker for studying the behavior of selenium removal efficiency as shown in Fig. The results illustrated that efficiency of selenium removal was decreased, by increasing the initial selenium ions concentration after 1 ppm. This was due to the fixed adsorbent dose the total available adsorption capacity was limited, which became saturated at a higher concentration.. Treating the sample of 1ppm the amount of selenium remains 0.0546 and the maximum removal of 94.54% was achieved.

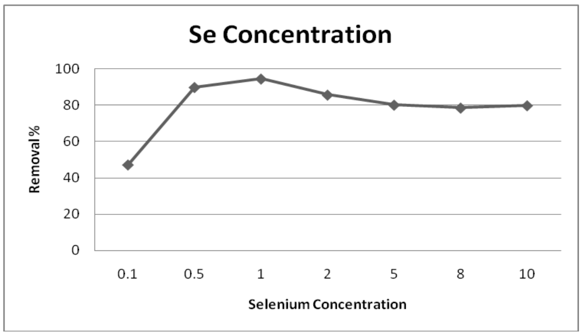


Fig. 4. Effect of Initial Selenium Concentration

IV. CONCLUSION

The results from the present study show the potential of Iron and Manganese bimetallic nanoadsorbent for the removal of selenium from water. The result of present study indicates that adsorption of selenium towards bimetallic nanoparticles is a chemical adsorption process. Bimetallic nanoparticles of iron and manganese were synthesized successfully which can remove about 95% of selenium from water within 60 minutes of contact time. Other optimized parameters were also determined from batch study such as 1mg/l of selenium concentration at pH of 8.5 with adsorbent dosage of 25mg removed above 90% of selenium from water. The equilibrium data were analyzed by using both Langmuir and Freundlich isotherms models. The R^2 values from both models were found to be (0.822 and 0.956) respectively. Equilibrium data fit very well with Freundlich isotherm equation. Maximum adsorption capacity of bimetallic nanoparticles calculated by Langmuir isotherm model was 25mg/g.

V. RECOMMENDATIONS

The effect of particles size on the selenium adsorption efficiency can be studied. In current study batch experiments were performed, in future column study analysis can be done using bimetallic nanoadsorbent. Adsorbent can also be used to remove other metalloid from water. Adsorbent is cost effective so it can be used on commercial scale. Adsorbent comparison study can be done with other adsorbent. Study can be done on interfering ions to enhance the removal efficiency of selenium on real water sample. Study can be done using same adsorbent for other toxic metals and metalloids.

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