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Research Paper

Magnetic Nanoparticle (Fe_3O_4) Impregnated onto Coconut Shell Activated Carbon for the Removal of Ni(II) from Aqueous Solution

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Abstract: The objective of this work is to study the adsorption of Ni(II) from aqueous solution using pure activated carbon (AC) and iron oxide modified activated carbon (AC- Fe_3O_4). The modification and adsorption process was monitored using FTIR and SEM. Equilibrium isotherms and kinetics were obtained and the effects of solution pH value, initial concentration and adsorbent dosage on the adsorption capacity of the adsorbent were studied in batch experiments. Equilibrium is well described by Langmuir and kinetics is found to fit pseudo-second-order type adsorption kinetics. Results show that modification of activated carbon with iron oxide improves its adsorption capacity.

Keywords: Nickel, Magnetic nanoparticle, Adsorption, Isotherm, Kinetics.

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Introduction

Industries such as metal plating, forging, mine, zinc base casting and silver refineries are continuously discharging effluents containing toxic heavy metals such as Ni(II), Zn(II), Hg(II), Cu(II) etc. from their industrial processes¹. Such ions gets a quick access into the human food chain after being accumulated in marine biomass which are in turn consumed by humans for sustenance.

Nickel is a common metal frequently used in different industries, vis., electroplating, storage batteries, and steel manufacturing etc.^{2,3}. In drinking water, nickel may causes health problems if found in amounts greater than the health standard set by the United State Environmental Protection Agency (EPA). The maximum concentration limit (MCL) for nickel has been set at 0.1 parts per million (ppm) because EPA believes this level would not cause any of the potential health problems⁴. However, effluents of different industries contain higher concentration of nickel than its acceptable limit. Although nickel is an essential micronutrient for animals and takes part in synthesis of

vitamin B₁₂, its higher concentration cause cancer of the lungs, nose, and bones and it may also cause nausea, rapid respiration, cyanosis, decreased body weight, heart and liver damage, skin irritation and dry cough⁵. Therefore, treatment of industrial effluent rich in Ni (II) before discharge becomes necessary.

Various treatment technologies have been developed for the purification of water and wastewater contaminated by heavy metals. Physiochemical methods are the most commonly used for the removal of heavy metal ions from industrial effluents. They include coagulation and flocculation, chemical precipitation, sedimentation, filtration, flotation, reverse osmosis, ultrafiltration, membrane and electro dialysis⁶. Although these methods are efficient for the treatment of water contaminated with heavy metals, they are very costly and therefore commercially unattractive⁷.

Adsorption onto activated carbon has an edge over the other techniques for water re-use in terms of flexibility, simplicity of design, ease of operation and scope of

metal recovery, but commercially produced activated carbon is also expensive. As a result of this and also in line with the global campaign of converting waste to wealth, researches nowadays are geared towards producing activated carbon mostly from agricultural wastes such as rice husk, neem leaf, banana peel, maize cobs etc. that have less or no competition from livestock industry, thereby making it cheaper and readily available⁸. However, the common drawback associated with such activated carbons is mostly their low adsorption capacities, hence, several modification methods are now being used to improve the performance of such activated carbons. In this present study, magnetic nanoparticle (Fe₃O₄) was impregnated onto coconut shell activated carbon and tested as an adsorbent for removal of Ni(II) from aqueous solution.

Material and Methods

Chemicals

All chemicals used were of analytical grade. They are nickel sulphate, ferrous chloride, ferric chloride, ammonia solution, acetone, hydrochloric acid, sodium hydroxide and ethyl alcohol supplied by Sigma Aldrich chemicals Pvt Ltd Bangalore, India, while dimethyl glyoxime was obtained from Qualigens Fine Chemicals Ltd., Mumbai, India.

Instruments

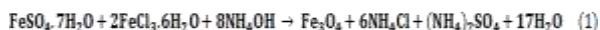
Instruments used for the collection of data are (i) pH meter (systronics made) for pH analysis (ii) UV-Visible spectrophotometer (Elico Model No: SL210) for analysis of metal concentrations in solution, while (iii) Scanning Electron Microscopy (emission current of 100μA by the Tungsten filament at a magnification of 15000x and an accelerator voltage of 20kV) and (iv) Fourier transform infrared spectroscopy (model: FTIR Bruker IFS 66V) were used for characterizations. Spectra obtained in the range of 400 to 4000 cm⁻¹ were analyzed.

Adsorbent

Coconut shells were obtained from shelling units and repeatedly washed with distilled water to remove dirt, dust and other surface impurities. The washed shells were dried in hot air oven at 120°C for 48h and grounded into particles for easy activation. The activation was carried out by soaking the particles into 18N concentrated sulphuric acid 1:2 (W/V) for 48h at room temperature to produce a carbon like material. These were then separated, washed several times with distilled water to eliminate excess acid and dried in hot air oven at 110°C. The dried material was then grounded using a mortar and pestle before being sieved using 100μm size mesh. This end product was referred to as activated carbon (AC). It was then stored in airtight container in a desiccator.

Preparation of AC-Fe₃O₄

Chemical precipitation technique was employed here⁹. In this process, 2.1g of FeSO₄.7H₂O and 3.1g of FeCl₃.6H₂O were dissolved under inert atmosphere in 80ml of double distilled water with vigorous stirring using a mechanical stirrer. While the solution was heated to 80°C, 10ml of NH₄OH solution (25%) was added. To ensure complete growth, 10g of the prepared activated carbon was added and reaction continued for 30 minutes. The resulting suspension was cooled down to room temperature and then repeatedly washed with distilled water to remove unreacted chemicals. The product was dried in an oven at 50°C for 2h, tested using a magnetic rod where it was found that all AC-Fe₃O₄ were attracted to the magnetic rod due to magnetic behaviour of iron. The reactions that occur in the production of AC-Fe₃O₄ can be represented using chemical equations (1) and (2).



Adsorbate Preparation

A stock solution of Ni (II) was prepared by dissolving 4.479g of NiSO₄.6H₂O in 1000 mL of double distilled water, acidified with nitric acid to prevent hydrolysis. Adsorption experiments were conducted to investigate the effect of adsorption parameters such as pH, adsorbent dosage, contact time and initial concentration on Ni(II) uptake by using AC-Fe₃O₄ as adsorbent.

Batch Adsorption Experiments

All adsorption experiments were carried out by batch techniques at room temperature on a mechanical shaker at 150rpm using 250ml capped conical flasks. The influence of pH, adsorbent dosage, initial adsorbate concentration and contact time on the performance of AC-Fe₃O₄ were evaluated. After equilibrium, the sample was centrifuged and the filtrates were analysed by a UV-visible spectrophotometer at 445 nm using the dimethyl glyoxime (DMG) method². The kinetic studies were carried out using a mechanical stirrer. The samples were withdrawn at predetermined time intervals and filtered. The amount of Ni(II) adsorbed per unit weight of AC-Fe₃O₄ adsorbent at time 't', q_t(mg/L) and percentage removal of Ni(II) was calculated using equations (3) and (4):

$$\text{Amount of Ni(II) adsorbed } (q_t) = \frac{V(C_o - C_e)}{m} \quad (3)$$

$$\text{Percentage removal of Ni(II)} = \frac{C_o - C_e}{C_o} \times 100 \quad (4)$$

Where C_o and C_e are the initial and equilibrium concentrations of Ni (mgL⁻¹) respectively, m is the mass of the adsorbent (g) and V is the volume of Ni (II) solution (L).

Results and Discussions

Characterization of Adsorbent

SEM Measurements

SEM measurements were carried out to determine the surface morphology of the parent activated carbon (AC), magnetic nanoparticle coated activated carbon before adsorption of Ni(II) ions (AC-Fe₃O₄) and magnetic nanoparticle coated activated carbon after adsorption of Ni(II) ions (AC-Fe₃O₄-Ni(II)). As shown in Fig. 1a, the parent AC has porous structure with abundant macrospores, Fig. 1b shows the parent AC completely covered with iron oxide. Fig. 1c shows the SEM image of AC-Fe₃O₄ after adsorption of Ni(II). Compared to Figure 1b, more particles are present on the surface of AC-Fe₃O₄ which are Ni(II) ions. This is as a result of the magnetic behavior exhibited by the iron oxide particles, creating more negative charges. The positively charged Ni(II) ions will in turn be electrostatically attracted to the adsorbent.



Figure 1: SEM image of (a) AC, (b) AC-Fe₃O₄, and (c) AC-Fe₃O₄-Ni(II)

FTIR Characterizations

The FTIR spectra of the parent activated carbon (AC), magnetic nanoparticle coated activated carbon before adsorption of Ni(II) ions (AC-Fe₃O₄) and magnetic nanoparticle coated activated carbon after adsorption of Ni(II) ions (AC-Fe₃O₄-Ni(II)) were all detected in the range of 4000 – 400cm⁻¹ and analyzed. The FTIR spectra of the parent AC and AC-Fe₃O₄ are shown in fig. 2a and b. The spectrum of the parent AC displayed a broad band at about 3441.73cm⁻¹, which was attributed to the stretching vibrations of the –OH groups with a minor contribution of –NH functional groups. The bands at 2340.60cm⁻¹ ascribes to C-N stretching in cyanide group. The bands at 1631.23cm⁻¹ can be assigned to symmetric and asymmetric stretching vibrations of the C=C group. The 1209.15cm⁻¹ band was attributed to the vibration of the C-O group. The peak around 648.49cm⁻¹ can be assigned to the bending modes of the C-H group. The band at 539.66cm⁻¹ is associated with out of plane aromatic ring deformation vibrations that is quite common for activated carbon.

Comparing the two spectra of fig. 2a and b, shows that there were various functional groups detected on the surface of AC-Fe₃O₄ as shown in fig. 2b. Emphasis was given to the newer peak at 619.63cm⁻¹ related to the Fe-O group, likewise the peak around 3415cm⁻¹ was

assigned to the –OH group on the surface of the magnetite.

Analyzing the spectra in figure 2c shows that the band corresponding to hydroxyl group has shifted to 3423.27cm⁻¹, due to the fact that hydroxyl groups are likely to participate in Ni(II) ion adsorption¹⁰.

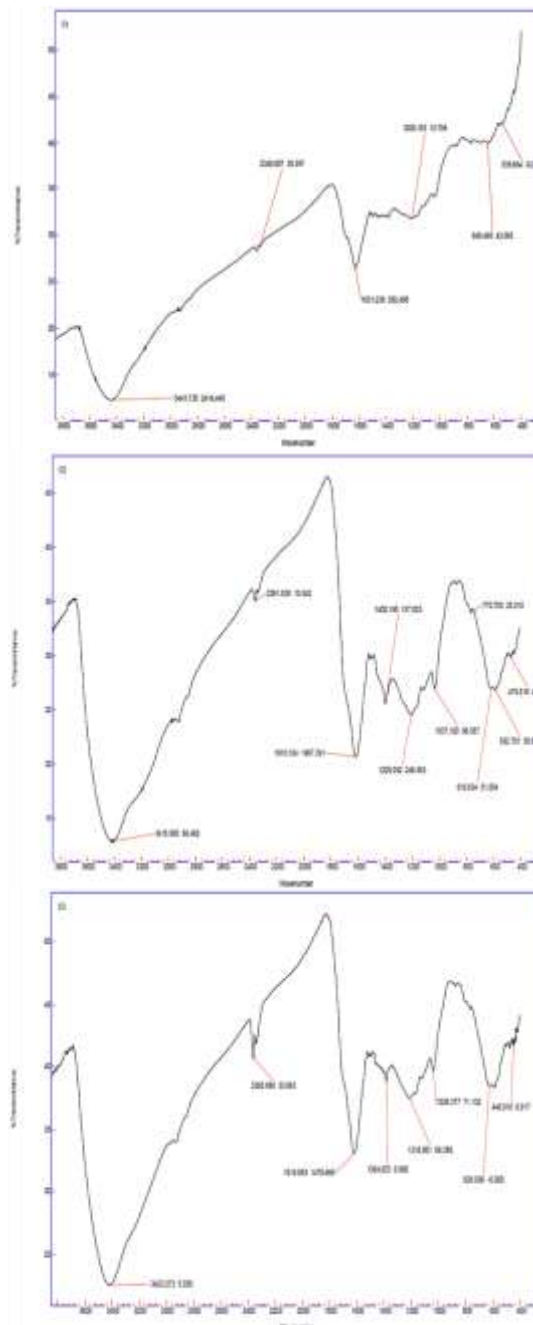


Figure 2: FTIR Spectra of (a) AC, (b) AC-Fe₃O₄, and (c) AC-Fe₃O₄-Ni(II)

Influence of pH

pH of aqueous solution is an important controlling parameter in the adsorption process and thus the influence of pH on the adsorption of Ni(II) ions by AC

and AC-Fe₃O₄ has been studied over the range of 2-7 as shown in figure 3. It was observed that between pH of 2-4, adsorption was low, at pH of 5, it becomes optimal while, adsorption remains virtually constant between the pH of 6-7. This was attributed to the fact that, at low pH of 2-4, the adsorbent surface is completely covered by H⁺ ions and Ni(II) ions cannot compete with them for ion exchange sites, at pH of 5, there are less H⁺ ions, hence Ni(II) ions can be exchanged with the exchangeable cations and also be adsorbed at the negatively charged sites of AC-Fe₃O₄, while adsorption remains virtually constant after the pH of 5 due to precipitation of Ni(II) as Ni(OH)₂¹¹⁻¹³.

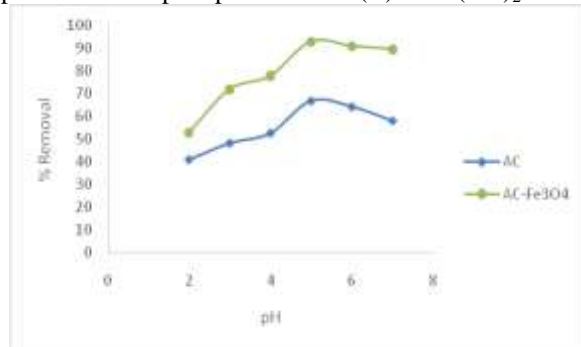


Figure 3: Influence of pH on the % removal of Ni(II) ions

Influence of initial Ni(II) concentration

This was done by varying the initial Ni(II) Concentration from 50 – 300ppm, while maintaining all other conditions. It was observed that as the initial Ni(II) concentration increases, adsorption decreases. The reason for this can be explained using the adsorbate/adsorbent ratio. At low concentration, the adsorbate/adsorbent ratio is less and there exist more available sites for adsorption. But at higher concentration, the ratio increases and the available sites becomes saturated, thereby decreasing the rate of adsorption¹⁴.

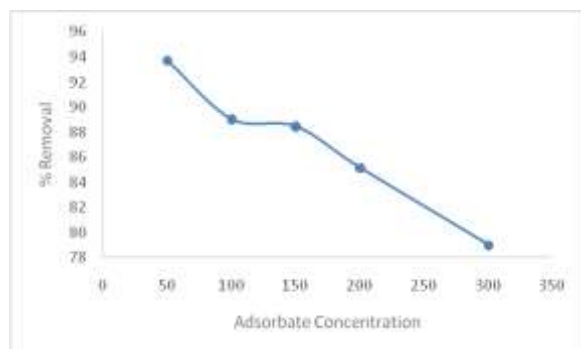


Figure 4: Influence of adsorbate concentration on the % removal of Ni(II) ions

Influence of adsorbent dosage

This was done by varying the adsorbent dosage from 0.1 to 0.6g in 50ml and 100mgL⁻¹. The result shows increased adsorption with increase in the amount of adsorbents. This can be explained by a greater availability of exchangeable sites or surface area at higher amount of the adsorbent. Another possible reason could be due to the fact that the concentration of nickel was fixed while the adsorbent dosage was increased. Therefore, as the dosage increased, the ratio of number of adsorption sites to the number of heavy metal ions would increase¹⁵.

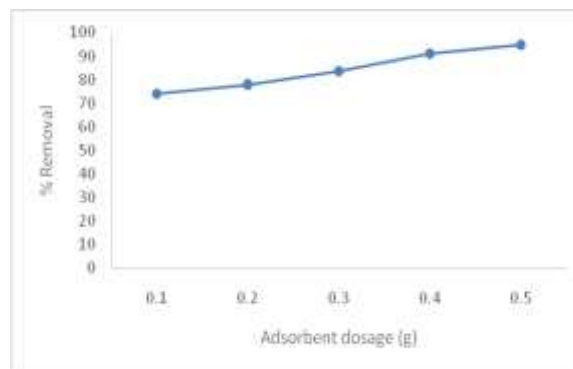


Figure 5: Influence of adsorbent dosage on the % removal of Ni(II) ions

Adsorption Isotherm

The study of adsorption isotherm is fundamental, and plays an important role in the determination of the maximal capacity of adsorbents. Langmuir and Freundlich isotherm models were used to assess the different isotherms and their ability to correlate experimental data.

Langmuir Isotherm

The Langmuir isotherm is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface¹⁶. The Langmuir equation may be written as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (5)$$

Where, C_e is the equilibrium concentration in liquid phase (mg/L), q_m is the monolayer adsorption capacity (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of the adsorbent (mgg⁻¹) and K_L is the Langmuir constant. Figures 6 shows linearized Langmuir isotherm for AC-Fe₃O₄. The more the R^2 value approaches unity, the more fitted the adsorption is to Langmuir isotherm.

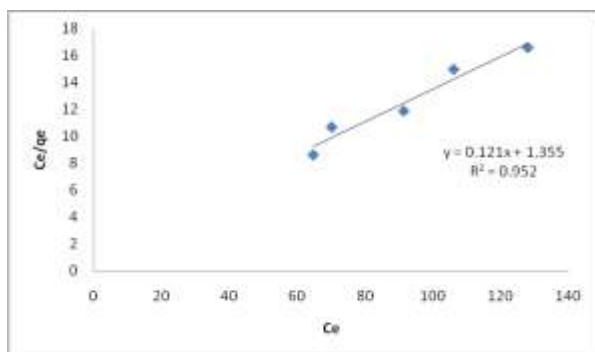


Fig.6: Langmuir isotherm for nickel adsorption onto AC-Fe₃O₄

Freundlich Isotherm

The Freundlich isotherm is an empirical equation that assumes heterogeneous adsorption due to the diversity adsorption sites¹⁷. The Freundlich equation may be written as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{6}$$

Where, q_e is the same with Langmuir's, C_e (mgL⁻¹) is the equilibrium concentration of the solute in the bulk solution, K_f is a constant indicative of the relative adsorption capacity of the adsorbent and n is a constant indicative of the intensity of the adsorption. The more the R^2 value approaches unity, the more fitted the adsorption is to Freundlich isotherm.

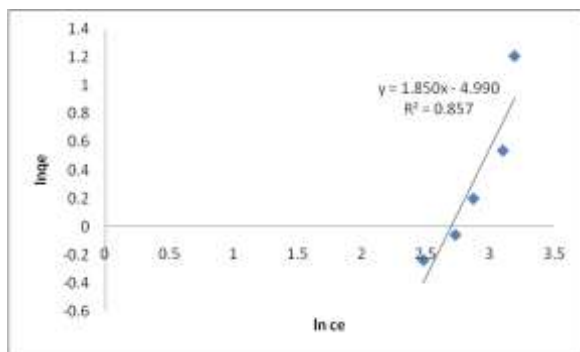


Fig.7: Freundlich isotherm for nickel adsorption onto AC-Fe₃O₄

Table 1: Isotherm Parameters for the removal of Ni (II) ions onto AC-Fe₃O₄

Langmuir constants			Freundlich constants		
q_m (mgg ⁻¹)	K_L (Lmg ⁻¹)	R^2	$K_F \times 10^{-3}$	$1/n$	R^2
8.223	0.089	0.952	6.802	1.850	0.857

Kinetic Studies

Due to their significance to adsorption process, two simplified kinetic models were used to examine the mechanism of the adsorption process. These are, the pseudo-first-order model and the pseudo-second-order model.

Pseudo-First-Order Model

The linear form of the integrated rate law for pseudo-first-order is expressed as¹⁸:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \tag{7}$$

Where q_e and q_t refer to the amount of the metal ion adsorbed (mmol/g) at equilibrium time, t (min) respectively and k_1 is the equilibrium rate constant of pseudo- first- order adsorption. Values for K_1 and R^2 obtained from the plot are presented in Table 2.

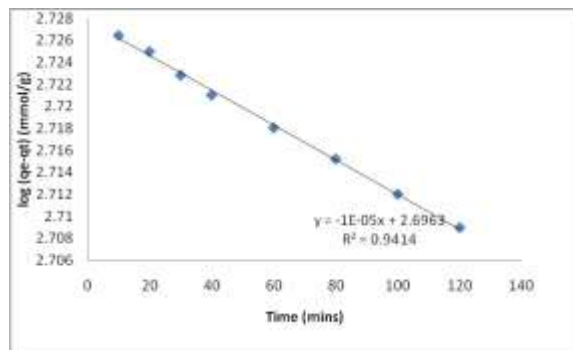


Fig. 8: Linear plot of pseudo-first-order equation for Ni(II) adsorption onto AC-Fe₃O₄

Pseudo-Second-Order Model

The linear form of the integrated rate law for pseudo-second-order model based on equilibrium adsorption is expressed as¹⁹:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

Where, q_e , q_t and t are same with pseudo-first-order, while k_2 is the rate constant of second order adsorption. Both the values for rake constant and correlation coefficient obtained from the plot are presented in Table 2.

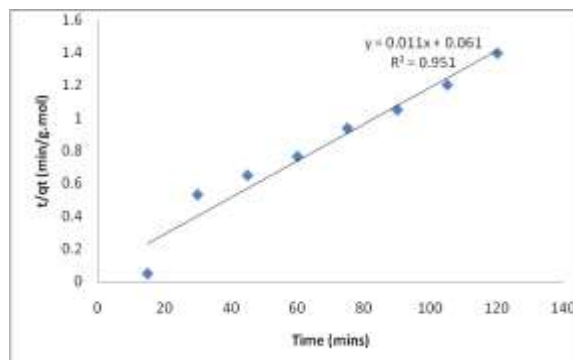


Fig. 9: Linear plot of pseudo-second-order equation for Ni(II) adsorption onto AC-Fe₃O₄

Table 2: Calculated parameters for pseudo- first order and pseudo-second models of Ni(II) ions adsorption onto AC-Fe₃O₄

Pseudo-first-order			Pseudo-second-order		
K ₁ (min ⁻¹)	q _e	R ²	K ₂	q _e	R ²
2.305	495.79	0.9414	2.066	89.49	0.9513

Conclusion

Results obtained showed that modification of activated carbon (AC) with iron oxide (Fe₃O₄) enhanced the adsorption of Ni(II) from aqueous solution. Adsorption of Ni(II) was found to be dependent on pH, initial concentration and adsorbent dosage. The experimental data for the adsorption of Ni(II) onto AC-Fe₃O₄ fits well with Langmuir isotherm than Freundlich isotherm. Kinetics of adsorption was found to follow pseudo-second-order model, an indication that the adsorption process was controlled by chemisorption. The study forecasts that waste water treatment, most especially heavy metals removal could give better results when conducted using iron oxide modified activated carbon than pristine activated carbon.

Acknowledgements

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