



Application of Iron Nanoparticle Coupled with Modified Orange Peel (FeNps/MOP) in Removal of Nickel from Water

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Abstract Iron nanoparticle coupled modified orange peel (FeNps/MOP) adsorbent was successfully synthesized using co-precipitation method. The structure and morphology of the adsorbent were studied during and after production using Fourier Transformation Infrared Spectroscopy (FTIR) and Scanning Electrode Microscopy (SEM) respectively. Both results confirmed the successful coupling of FeNps and MOP. The adsorption parameters such as contact time, adsorbent load, pH and temperature were all optimized. Under optimum condition, the adsorbent has the capacity to reduce or remove about 90% of Ni²⁺ out of water.

Keywords orange peel; chemical modification; adsorption capacity

Introduction

Anthropogenic activities have led to serious ills to our ecosystem with deserved health hazard. Heavy metals are the commonly released pollutants as result of their wide industrial usage, unlike organic pollutants, the majority of which are susceptible to biological degradation, but heavy metal ions do not degrade into harmless end products [1]. Heavy metals contamination exists in wastewater of many industries such as metal plating, mining operations, surface finishing industry, tanneries, paper and pulp industries, fertilizer and pesticide industry, radiator manufacturing, smelting, energy and fuel production, aerospace and atomic energy installation, alloy industries, electroplating and batteries industries [2, 3]. Heavy metals are toxic even at very low concentration and their toxicity can result to Acute exposure to heavy metals can result to aches, nausea, vomiting, weakness, pulmonary edema and diarrhea while chronic exposure result to respiratory cancers, damage of gastrointestinal tract, kidneys, liver, blood cells in some cases death [4]. The danger resulted as a presence of heavy metals is the stability of their ions in exterior medium and solubility in water. Unlike organic pollutants, majority of which are susceptible to biological degradation, heavy metals do not degrade into harmless products [5]. Therefore, it is necessary to find an efficient and cost effective method of removing heavy metal pollutants from wastewater before discharging into ecosystem.

Traditional methods like chemical precipitation, coagulation, solvent extraction, ion exchange electrolysis, reverse osmosis sedimentation, electro-dialysis, biological processes etc., have been used for the removal of heavy metals



from waste water over time [6][7]. These traditional methods are extremely expensive, require a lot of energy and chemicals, sometimes ineffective, especially when metals are present in solution at very low concentrations, and cannot be used on large scale applications [4, 7].

Adsorption is a trendy and economical water treatment process that has been used to remove different types of heavy metals due to its efficiency, simplicity, potential metal recovery and environmental friendliness [7]. The biomass derived from agricultural waste has a particular attractive attention as adsorbents because of their chemical stability and high reactivity resulting from the presence of repetitive functional groups in cellulosic chain such as content of cellulose, pectin (galacturonic acid) hemicellulose and lignin [3], [8] These components bear various polar functional groups including carboxylic and phenolic acid group to be involved in metal binding and are biopolymers admittedly associated to the removal of heavy metals. As a low-cost adsorbent, orange peel is an attractive option for the adsorption removal of dissolved metals [8].

Unfortunately, during the removal of the heavy metal, some functional group tends to produce permanent bond with metal thereby rendering none reusable the bioadsorbent after first or second used. To eliminate these challenges, the research intends to introduce magnetite (Fe_3O_4) Nanoparticle on the bioadsorbent. The choice of magnetic Nanoparticle was due to relatively large the surface area, non-toxicity [9][10], fast ability to remove both organic and inorganic pollutant [9][10][11], excellent porosity, easy method of preparation, good thermal stability and excellent magnetic properties [10, 11]. Lastly Magnetic nanoparticles can be easily separated from aqueous samples by applying an external magnetic field [9][10].

Materials and Methods

Chemicals and Instruments

All the components were analytical reagent-grade and used as supplied. Iron (III) chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), Iron (II) sulphate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Sodium hydroxide (NaOH) hydrochloric acid (HCl), Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were purchased from Sigma-Adrich. Double distilled deionized water was used throughout experiments. And pH meter (HACH-HQ-USA) for control pH solution (± 0.01). For determination of nickel residual concentrations applied UV-Visible spectrophotometer (T60, PG instrument).

Preparation of Modified Orange Peel (MOP)

Orange peel was obtained from Umyu campus and was cut in to small pieces, washed several times with double distilled water to remove sand and any other foreign substances that may interfere with the production and dried at 60°C . The product was crushed and sieved to obtain an average particle size lower than 0.45 mm and the fines powder was treated with sodium hydroxide and calcium chloride solutions to improve the capacity of metal adsorption. Finally, the modified OPP (MOP) was washed until the solutions reached a pH value of 7.0, and then dried.

Preparation of Iron Nanoparticle Coupled with Modified Orange Peel Powder (FeNps/MOP)

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (18.3 g) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (14.0 g) was dissolved in degassed hydrochloric acid (2 mol L^{-1} , 50 mL) in a flask at room temperature under sonication. All the solutions were degassed using a vacuum pump and filled with nitrogen gas. The contents of the flask were stirred for 10 min before adding aqueous ammonia (28%, 80 mL) and 3 g of MOP into the mixture.

The mixture was stirred at 80°C for 30 minutes using magnetic stirrer in order to ensure a good coupling between magnetite nanoparticle (Fe_3O_4) and orange peel powder (OPP). The mixture was allowed to cool. The resulting product was filtered, sonicated until the pH stabilized and finally was dried at 50°C for 24 hours and stored in a suitable container for test use.

Instrumental Characterization of the FeNps/MOP

The structural changes during the production stage were observed under Fourier transform infrared spectroscopy (FTIR) while the surface morphology was studied using Scanning electron microscope (SEM).



Nickel Salt Solution Adsorption Optimization

At first standard stock solution of Nickel salt at a 1000 mg/L was prepared by dissolving required amount in distilled water shaken for constant speed of 220 rpm using shaker to ensure effective solubility of the salt. Then stock solution diluted by distilled water to prepare different concentrations. The experiments of Nickel salt adsorption onto FeNps/MOP was carried out by batch adsorption method. All experiments were done on 100 mL conical flasks containing certain amount of adsorbent and 50 mL of Nickel Salt solution. The impact of pH on adsorption Nickel salt solution was studied in the range of 2–10 with initial concentration of 70 ppm and contact time of 60 min. The pH of the solutions was adjusted with hydrochloric acid (0.1 M HCl) and sodium hydroxide (0.1 M NaOH). Effect of contact time and temperature were also studied.

Results and Discussion

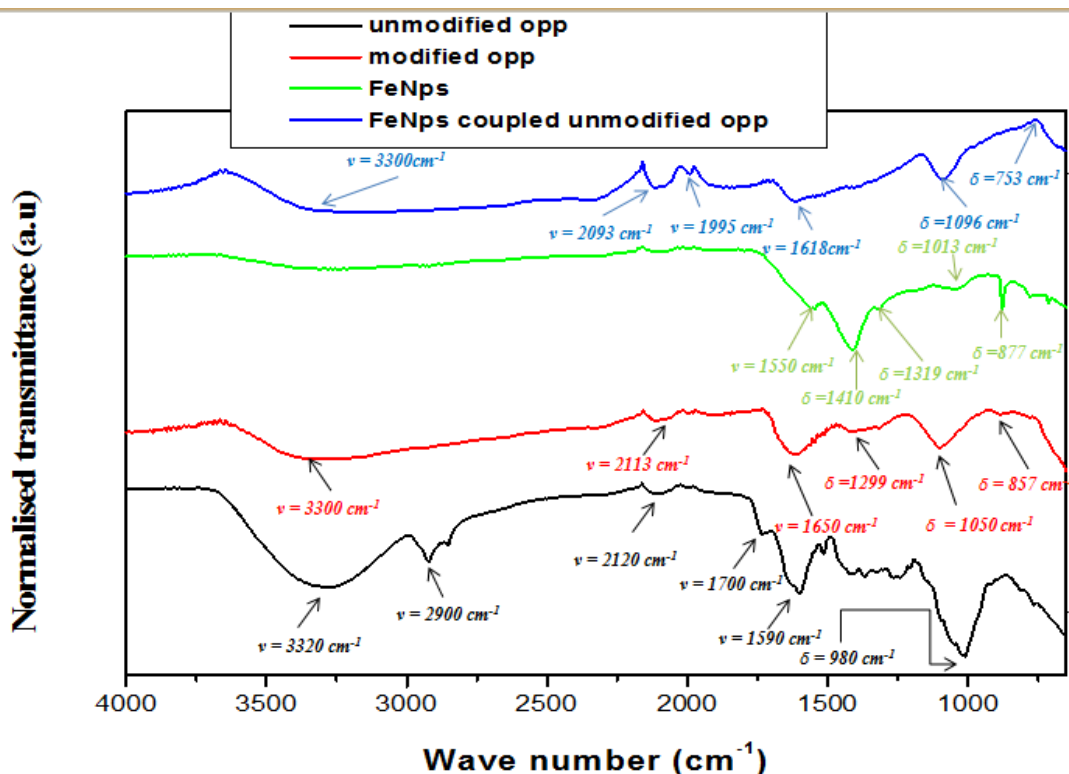


Figure 1: FTIR spectra of OPP, MOP, FeNps and FeNps/MOP

Unmodified Orange Peel Powder

From the spectra above, various peak could be observed corresponding to various functional groups on unmodified orange peels. The peaks includes 3320 cm^{-1} corresponding to O-H stretching vibration of cellulose hemicelluloses, pectin, lignin and absorbed water, peak at 2900 cm^{-1} attributed to C-H stretching and bending vibrations of methyl, methylene and methoxy groups, The peak at 1700 cm^{-1} corresponding to stretching vibration of C=O bond due to non-ionic carboxyl groups (-COO, -COOR), assigned to carboxylic acids or esters in pectin. The peak at 1590 cm^{-1} can be assigned to the C=C bond of benzene ring structure in lignin while the peak at 980 cm^{-1} refers to the glycoside bond (C-O-C) mainly existing in cellulose, hemicelluloses and pectin [12].



Modified Orange Peel Powder

Spectrum corresponding to modified orange peel powder shows some resemblance with unmodified orange peel powder spectrum with a little change in peak position or reduction in peak intensity. It could be observed that the peaks at 3320cm^{-1} , 2120cm^{-1} and 1590cm^{-1} in unmodified spectrum had witness peak intensity reduction as well as shift in wavelength to 3300cm^{-1} , 2113cm^{-1} and 1650cm^{-1} respectively in modified spectrum while Peak at 2900cm^{-1} , 1700cm^{-1} 980cm^{-1} disappeared in the modified orange peels spectrum. New peaks could be observed at 1299 , 1050 and 857cm^{-1} assigned to bending mode vibration of methyl, methylene and methoxy groups. These changes confirmed successful modification of the orange peels.

Iron Nanoparticle (FeNps)

The two intense peaks observed at 877 cm^{-1} was attributed to the stretching vibration mode associated to the metal oxygen Fe-O bonds in the crystalline lattice of FeNps, similar to the result reported by Yagner et al., (2014). The band centered at 1550 cm^{-1} are related to the presence of hydroxyl groups and attributed to OH – bending and O-H stretching believed to be from NaOH used during production. The peaks at 1410 , 1319 , 1013 and 877 cm^{-1} correspond to the bending mode vibration associated with FeNps.

FeNps Coupled modified orange peels powder

The spectrum shows mixture of peaks from Modified orange peel spectrum and FeNps spectrum. The presence of these peaks signifies successful coupling of FeNps with modified orange peels.

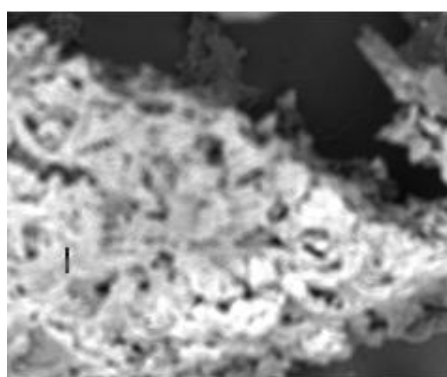


Fig: 2A

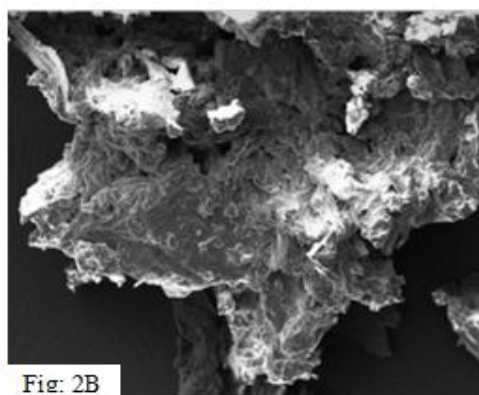


Fig: 2B

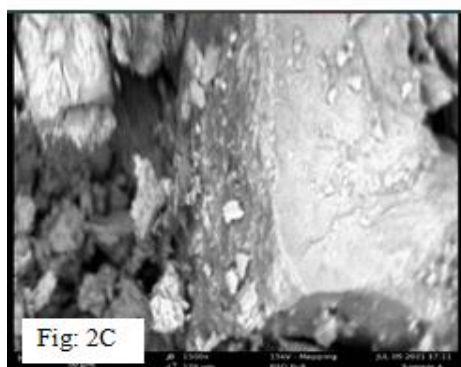


Fig: 2C

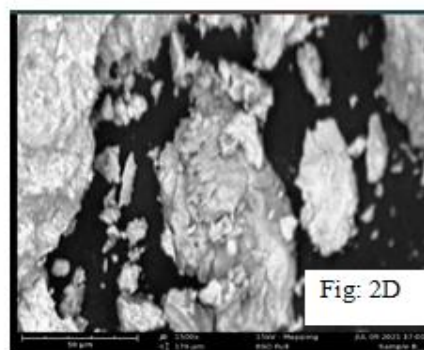


Fig: 2D

Figure 2: The Scanning electron microscope (SEM) images of (a) Unmodified orange peels powder (b) Modified Opp (c) FeNps (d) FeNps coupled unmodified orange peels powder



The surface morphology and texture of our adsorbent were viewed under scanning electron microscope (SEM) at 500X magnification shown in fig 2a-d. The SEM images in the fig 2a above of unmodified orange peels powder, the porosity and uniform surface can be observed from the image while the texture shows well-structured layer with defined cavities and channels.

Increase in size of pores and compacted structure can be observed after modification of the orange peels. The compaction of the texture indicated increase in surface area as well ability of the modified orange peels powder to more absorption for heavy metals as reported by [4].

Huge crystal structure typical of FeNps can be seen clearly on the image of this structure was responsible for the magnetic property of FeNps as reported [2]. The coupled image shows clear crystal and excellent porosity seen in both FeNps and modified Opp.

pH Optimization

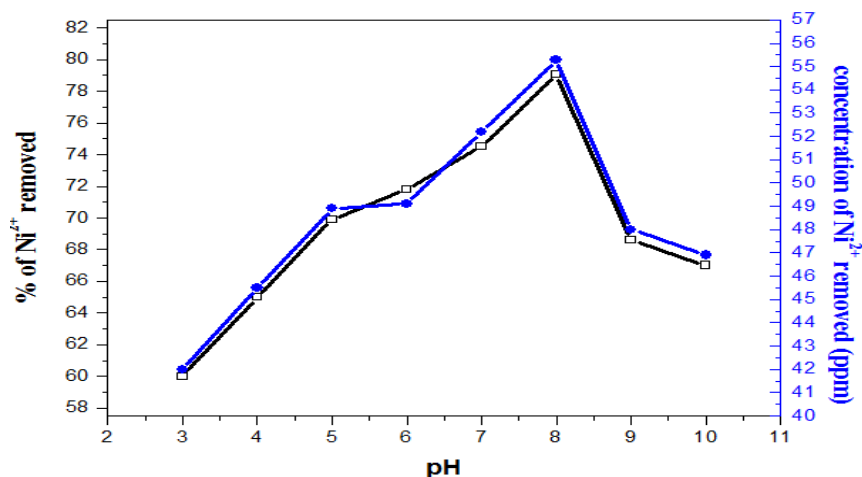


Figure 3: pH study using analyte concentration of 70ppm, contact time of 60min

The figure 3 shows that with increasing pH from 3 to 8, the adsorption efficiency increases and then decreases at higher pH, the minimum adsorption was recorded at pH 3 representing 61.3% (42.91 ± 0.7 ppm) removal while the maximum performance was recorded at pH 8 with 79.05% (55.34 ± 0.6 ppm). The increase in percentage removal of the metal ions may be explained by the fact that at higher pH, the functional groups in the adsorbent surface were deprotonated and become negatively charged; hence attraction between the positively charged metal ions occurred [13].

Contact Optimization

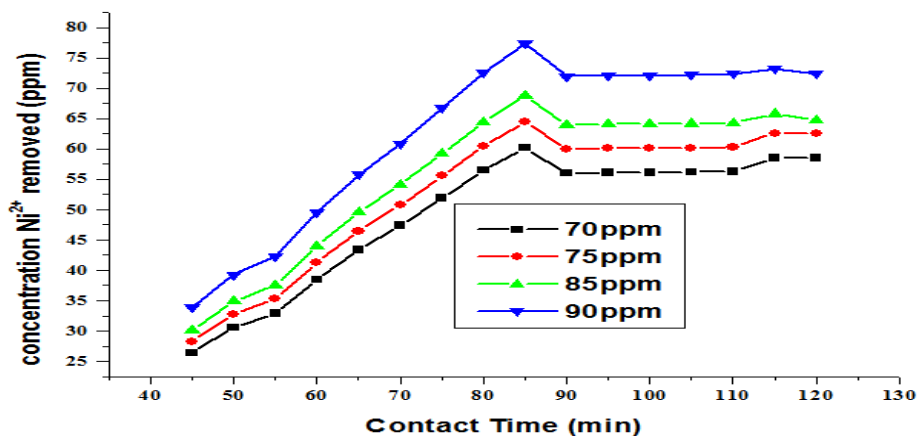


Figure 4: The effect of varying contact on the performance of FeNps/MOP toward removal of Ni²⁺



Contact time is one of the factors effecting the development of surface charges at the solid solution interface. A rapid uptake of pollutants and establishment of equilibrium in a short period signifies the efficiency of the adsorbent for its use in wastewater treatment. Moreover, the adsorbate concentration and contact time between adsorbent and adsorbate species plays an important role in the process of removal of pollutants from water and wastewater by adsorption at a particular temperature and pH [14]. Therefore effect of the influence of contact time for nickel salt adsorption onto synthesized adsorbent at different concentrations (70-90 ppm) at pH 8 was investigated. The graph (fig 4) trends indicate 85 min to be the optimum contact time for effective removal of the analyte. The attaining of saturation point at the same time interval for different initial concentration indicate nickel adsorption completely depends upon the number of active sites which are capable of making complex with the metal ion [2, 13].

Adsorbent Dose Optimization

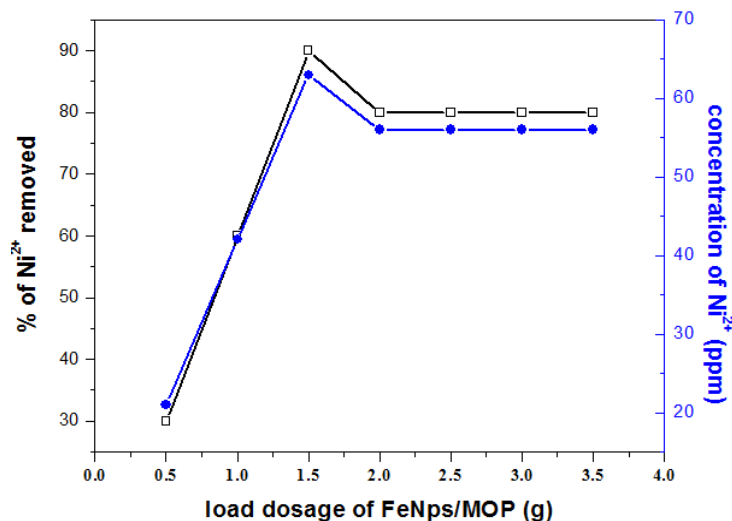


Figure 5: Effect of FeNps/MOP dosage on Ni²⁺ removal

The availability and accessibility of adsorption site is controlled by adsorbent dosage. The effect FeNps/MOP dosage in the removal of 70 ppm Ni²⁺ was investigated by varying the load dosage from 0.5 g to 4 g. The result (Fig 5) shows that increased adsorbent loading increased the metal ion percentage removal. The removal of Ni²⁺ attained maximum removal at 1.5 g were 90% (63 ppm) was successfully removed. Further increase in adsorbent dosage brought no increase in adsorption.

Temperature Optimization

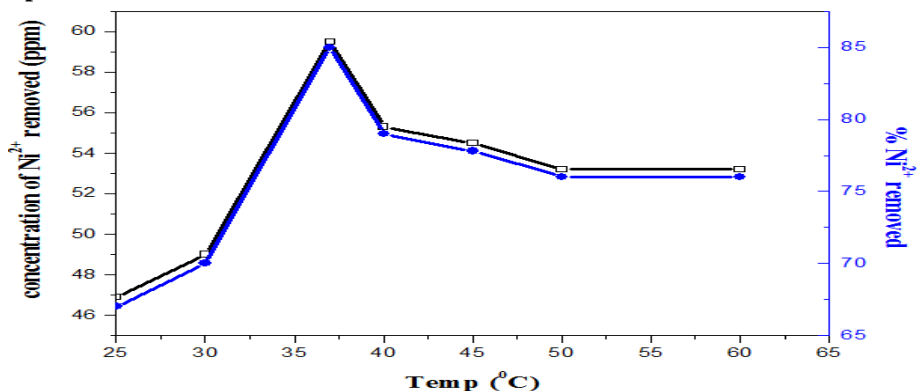


Figure 6: The effect of temperature on adsorption efficiency of FeNps/MOP

From result (fig 6) increase in temperature above 37°C resulted in decrease in both adsorption efficiency and removal of Ni²⁺ (70 ppm) on FeNps/MOP. This indicated the adsorption behavior was not temperature depended.

The trends indicate that the Ni^{2+} adsorption on FeNps/MOP was exothermic. The result was in conformity with result obtained by [4, 11].

Table 1: The reusability and stability data

Number trial	initial concentration (Ci) ppm	concentration at equilibrium (Ce) ppm	% removal of Ni^{2+}	Type of adsorbent
1st trial	40	3.2	92	adsorbent A
	50	5	90	adsorbent B
	70	6.3	91	adsorbent C
2nd trial	40	3.6	91	adsorbent A
	50	5	90	adsorbent B
	70	7	90	adsorbent C
3rd trial	40	4	90	adsorbent A
	50	6	88	adsorbent B
	70	7.7	89	adsorbent C
4th trial	40	15.6	61	adsorbent A
	50	20	60	adsorbent B
	70	32.2	54	adsorbent C
5th trial	40	31.6	21	adsorbent A
	50	33.5	33	adsorbent B
	70	38.5	45	adsorbent C

Reusability and stability of FeNps/MOP

The FeNps/MOP were grouped into adsorbent A, adsorbent B, adsorbent C. Each adsorbent reusability and stability was estimated by recording the percentage removal of assigned concentration Ni^{2+} at optimum adsorption condition. After every used the adsorbent were placed into the 0.1N NaOH solution and shaken for an hour. The adsorbent was then filtered and washed with dilute acid and deionized water. The washed adsorbents were allowed to dry at room temperature for 2days before reused.

From the result, (table 1) the 1st trial recorded 92, 90 and 91% successful Ni^{2+} removal. The excellent performance was also recorded in 2nd and 3rd trials with almost the same percentage removal of Ni^{2+} proved the reusability of FeNps/MOP material. The ability of the retained 21 and 33 and 45% its performance even after 10 days of used indicated an excellent stability of the produced adsorbate.

Conclusion

FeNps/MoP was successfully produced using co-precipitation method. Under optimum condition the composite show good Ni^{2+} removal due to presence of functional group capable binding with Ni^{2+} . The composite show excellent reusability and stability if properly stored.

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