

Evaluation of Efficiency of Nickel Removal from Simulated Paint Effluent through Coagulation-Flocculation Using Ferric Sulphate and Chitosan

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Abstract

Coagulation-Flocculation of Nickel (II) ions from simulated wastewater using ferric sulphate and chitosan has been investigated. The chitosan extraction was done in four steps; pre-treatment, demineralization, deproteinization and deacetylation steps. The shrimp shell wastes were found to contain 41.67% mineral content, 37.67% protein content, 20.67% chitin and 7.00% chitosan respectively. Physicochemical analysis of the sample revealed that shrimp shells (wastes) are a good source of chitosan with moisture content (1.60%), ash content (0.52%), crude fibre content (3.50%), fat content (0.32%), protein content (17.50%), carbon content (16.46%), nitrogen content (2.80%) and degree of deacetylation (57.10%). FTIR revealed absorption bands within the 1420-603 cm⁻¹ region which confirmed the presence of CH₃, CH₂ and CH groups as well as the primary and secondary OH groups, attached to the pyranose ring, and the oxygen atoms in ether groups. The coagulation-flocculation studies were done while checking for the influence of some parameters such as pH, settling time, temperature, coagulant dosage and concentration of the heavy metal ion. These factors individually and collectively have a great influence on the coagulant's optimum performance. The results obtained from the study showed that chitosan coagulant was more effective than the ferric sulphate in water treatment.

Keywords: Chitosan, Deacetylation, Demineralization, Deproteinization, Nickel, Wastewater

1. Introduction

The demand for potable water has increased by several factors due to increased economic activity, rapid industrialization and robust population growth. Globally, the threat posed on water resources is not only by poor management and over-exploitation, but also by ecological degradation (Mahmood, Salman & Syed, 2010). As reported by Varsha and Jay (2012), the cost of water treatment is increasing, and the quality of rivers is deteriorating due to land development. Due to indiscriminate disposal of industrial and domestic wastes, clean water is becoming scarce especially in developing countries such as Nigeria. The presence of paint industries in urban areas has caused a high level of pollution of land, water and air, because of their waste discharge. Paint industry waste discharge into the environment

causes unbearable odours, loss in soil fertility due to chemical spills and contamination of water bodies with heavy metals (Abia, Harsfall & Didi, 2003).

Heavy metals are elements with an atomic density greater than 5.0g/cm^3 . They are also referred to as trace elements and are the metallic elements of the periodic table (Salem, Eweida & Farag, 2000). They are among the most persistent pollutants in wastewater (Srivastava & Majumder, 2008). The most common toxic heavy metals in wastewater include arsenic, lead, mercury, cadmium, chromium, copper, nickel, silver, and zinc. The release of high amounts of heavy metals into water bodies creates serious health and environmental problems and may lead to an upsurge in the treatment of wastewater. The two main sources of heavy metals in wastewater are natural and human sources. Heavy metals occur in small amounts naturally and may enter into aquatic system through soil erosion, volcanic activities, leaching of rocks, airborne dust, forest fires and vegetation (Fernandez & Olalla, 2000; Ogoyi, Mwita, Nguu & Shiundu, 2011) while the human factors include municipal discharge, domestic or household discharge, industrial processes like metal finishing and electroplating processes, mining extraction operations, textile industries and nuclear power. Their occurrence and accumulation in the environment are results of direct or indirect human activities such as rapid industrialization, urbanization and anthropogenic sources.

The persistence of heavy metals in wastewater is due to their non-biodegradable and toxicity nature (Jern, 2006). Some of the negative impacts of heavy metals on plants include decrease of seed germination and lipid content by cadmium, decreased enzyme activity and plant growth by chromium, the inhibition of photosynthesis by copper and mercury, the reduction of seed germination by nickel and the reduction of chlorophyll production and plant growth by lead (Gardea-Torresdey, Peratta-Videa, Rosa & Parson, 2005). The effects on animals include reduced growth and development, cancer, organ damage, nervous system damage and in extreme cases, death (Duruibe, Ogwuegbu & Egwurugwu, 2007). Due to the toxicity and non-biodegradability of heavy metals in wastewater and the adverse health impact, other contaminants such as pathogens, organic particles like feces, hairs, food, vomit, paper fibers, decomposing plant material, humus, and so on. There is need for adequate treatment of effluents before discharge to receiving water bodies.

Research in the wastewater treatment strategies in recent years has been focusing attention on the use of techniques such as adsorption, membrane filtration, chemical precipitation, coagulation-flocculation etc. (Chukwudi & Uche, 2008; Li, Li, Zhang & Liu, 2009). Adsorption has a relatively high capital cost, product recovery possibly requires a special and expensive extraction, adsorbent regeneration requires steam or vacuum source and used adsorbent may be considered a hazardous waste. In membrane filtration, there is fouling effect which leads to decrease in permeate flux, short membrane life-span, membrane with wide pores give poor separation performance for smaller particles. It is expensive to run and maintain. Chemical precipitation is very expensive and has a high energy cost. On the other hand, coagulation-flocculation is not expensive for there is a great reduction in the settling time of suspended solids. It is also efficient in removing fine particles that cannot be easily removed by other techniques (Carpinteyro-Urban & Torres, 2013).

According to Armenante (2004), coagulation is a chemical process that involves neutralization of charges in the particles thereby destabilizing the colloidal suspension and causing the particles to agglomerate. The particles can be mineral, organic or biological in nature. Flocculation process is one of the main stages in water and wastewater treatment. It

occurs when destabilized particles from the coagulation stage are mechanically induced to agglomerate into fast settling particles commonly called flocs. The agglomeration of the particles is due to velocity difference or gradient in the previously coagulated water. The agglomerates or flocs are ultimately removed by sedimentation or in some cases floatation (Bolto & Gregory, 2007). In wastewater treatment, coagulation-flocculation involves the addition of polymers that clump the small, destabilized particles together into larger aggregates so that they can be more easily separated from the water. The coagulation-flocculation process can be used as a preliminary or intermediary step between other water or wastewater treatment processes like filtration and sedimentation. The inorganic, organic and biomaterials that promote aggregation and sedimentation of suspended particles in solution are called coagulants and flocculants.

Ferric sulphate, a synthetic coagulant, is not cost effective for water treatment. It has been used in wastewater treatment where it has been prepared from waste chemicals. Chitosan is a natural biopolymer, which is extracted from crustacean shells or from fungal biomass. The high porosity of this natural polymer results in novel binding properties for metal ions such as cadmium, copper, lead, mercury and chromium (Varma, Deshpande & Kennedy, 2004). Some of the properties which are commercially attractive are natural decomposition, non-toxic to both the environment and human and having no side or allergic effects if implanted in the body.

Chitosan is partially deacetylated polymer, natural and water soluble derivative of cellulose with unique properties. It has a large amount of the crustacean exoskeleton as a by-product of food processing.

2. Materials and Methods

2.1. Materials

The raw material used for the synthesis of natural coagulant was the shrimp shells, purchased from Terminus market, Jos, Plateau State, Nigeria. The chemicals used were all of analytical grade. They included: ferric sulphate (MERCK 99.5%), hydrochloric acid (MERCK >99.8%), sodium hydroxide (MERCK 99.0%) and nickel nitrate (MERCK 99.0 – 101.0%).

2.2. Extraction of Crude Chitosan from Shrimp Shells

The extraction of chitosan was done in four steps: pre-treatment, demineralization, deproteinization and deacetylation steps. The shells obtained were washed thoroughly with distilled water and dried in an oven to a constant weight at a temperature of 30°C. Then, 300g of the sample was used in the extraction process. The dried shells were ground and soaked in 5% HCl (1:10 w/v) at approximately 30°C for 6 hours after which it was washed in the acid solution until no bubbles were seen. The sample was repeatedly washed with distilled water and dried to constant weight.

The dry demineralized shrimp powder was weighed and soaked in 10% NaOH solution (1:10w/v) at approximately 30°C for 12 hours after which the powder was washed thoroughly with distilled water until a neutral pH was obtained. The chitin obtained was then dried to constant weight and ground and screened with 75µm sieve.

The chitin obtained was deacetylated in 60% NaOH (1:10 w/v) for 24 hours at 30°C after which it was washed thoroughly with distilled water. The chitosan obtained was then dried to constant weight.

2.3. Physicochemical Analysis of The Samples

The AOAC procedures were used in conducting the physicochemical analysis of the samples. This was done so as to determine the sample's moisture, ash, crude fibre, fat, protein, carbon and nitrogen contents.

2.4. Waste water Analysis and Simulation

The metal ion concentration of the raw paint effluent collected from Jecca Paint Industries, Onitsha, Anambra State, Nigeria was analysed using the Atomic Adsorption Spectrophotometer (Varian 240/280). After which the simulated wastewater was prepared in such a way that its concentration was higher than the raw for an improved investigation. To simulate the contaminated wastewater, a known mass of nickel metal salt (Iron(iii) sulphate) was weighed and incorporated into 1000 ml of the distilled water. This was observed so as to simulate standard (wastewater) solution for treatment using the coagulant types respectively. The initial and final concentration of the solution as detected by the spectrophotometer was recorded. The simulation of the paint effluent was done so as to successfully investigate the coagulation/ flocculation of nickel ion only.

2.5. Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of the natural coagulant sample were taken by placing a very small amount of the samples on a Fourier Transform Infrared Spectrophotometer (Agilent Technologies CARY 630). The spectrum from each of the samples showing the functional groups present was then obtained.

2.6. Coagulation-Flocculation of Simulated Wastewater

The effects of five parameters were chosen as basis for process investigation. These were: pH effect ranges of 2,5,7,9 and 11, settling time effect, ranges from 20⁰, 40⁰, 60⁰, 80⁰ and 100⁰C temperature, coagulant dosage effect and initial metal ion concentration effect.

3. Results and Discussion

3.1. Crude Chitosan Content

Table 3.1 shows the content of the crude chitosan in the shrimp shells. The mineral content of the shells was found to be 41.67% whereas the protein content was 37.67%. Abdulwadud, Muhammed, Surajudeen, Abubakar and Alewo (2013) reported 51.62% mineral content and 9.99% protein content. The variation in percentage contents of mineral and protein can be due to the different water bodies in which these shrimps thrive in. As shown in Table 3.1 also, the shrimp shell wastes were found to contain 20.67% deacetylation, 7.00% crude chitosan, 37.67% deproteinization and 41.67% demineralization. Abdou, Nagy and Elsabee (2008) reported chitin and chitosan contents of 23.25% and 15.14% for mussel shells. According to them, the variation in percentage content of chitosan can be attributed to the primary source. The isolation process from different sources is

affected by the creatures where chitin is found, and it is in different percentages depending on the habitat (Muzzarelli, 1997; Kumar, 2000).

Table 3.1: Crude Chitosan Content

Shrimp Shells	Demineralization (%)	Deproteinization (%)	Deacetylation (%)	Crude Chitosan Content (%)
	41.67	37.67	20.67	7.00

3.2. Physicochemical Analysis

The results of physicochemical analysis of the sample are shown in Table 3.2. It revealed that shrimp shells (wastes) are a good source of chitosan with moisture content (1.60%), ash content (0.52%), crude fibre content (3.50%), fat content (0.32%), protein content (17.50%), carbon content (16.46%), nitrogen content (2.80%) and degree of deacetylation (57.10%). The results of the analysis gave an insight to the percentage composition of the sample used and were close to those obtained by other researchers (Islam, Masum, Molla, Rahman, Shaikh & Roy, 2011; Kalut, S.A., 2008; Khanafari, Marandi & Sanatei, 2008; Muhammed, Alewo, Joseph & Kenneth, 2012).

Table 3.2: Physicochemical Analysis of Crude Chitosan

Parameters	Content (%)
Moisture	1.6
Ash	0.52
Crude Fibre	3.5
Fat	0.32
Protein	17.5
Carbon	16.46
Nitrogen	2.8
Degree of Deacetylation (%)	57.1

3.3. FTIR Spectra of Sample

The spectra of the samples are shown in Figures 3.1 to 3.3 respectively. Several researchers have described and interpreted the infrared spectra of chitin and chitosan respectively (Brugnerotto, Lizardi, Goycoolea, Arguelles, Desbriere, & Rinaudo, 2001; Marguerite Rinaudo (2006)). According to Marguerite (2006), spectra of chitin (and chitosan) samples display a series of very sharp absorption bands because of the high crystallinity of the samples, hence, typical of polysaccharides. For both chitin and chitosan, the C=O stretching region of the amide group is shown between 1600 and 1110 cm^{-1} . The amide I band is split at 1656 and 1621 cm^{-1} .

Different stretching vibration bands were observed in the range, 3425 - 2881 cm^{-1} which is related to $\nu(\text{N-H})$ in $\nu(\text{NH}_2)$ assoc. in primary amines (Shigemasa, Matsuura, Sashiwa, & Saimoto, 2006). The band at 3425-3422 cm^{-1} could be assigned to $\nu(\text{N-H})$, $\nu(\text{O-H})$ and $\nu(\text{NH}_2)$. The presence of methyl group in NHCOCH_3 , methylene group in CH_2OH and methyne group in pyranose ring was confirmed by the corresponding stretching vibrations of these groups in the range, 2921-2879 cm^{-1} .

The absorption bands within the 1420-603 cm^{-1} region confirmed the presence of CH_3 , CH_2 and CH groups as well as the primary and secondary OH groups attached to the pyranose ring, and the oxygen atoms in ether groups. Moreover, for chitin, absorption bands at 1262-1205 cm^{-1} were observed. This could be assigned to complex vibrations of NHCO , with characteristic frequencies for secondary amides only. For the chitosan, the absence of some characteristic bands can be attributed to the effect of deacetylation process. Also, the changes in the region 1667–1597 cm^{-1} were due to the differences in IR absorption characteristics of the free amine and the amine salt. A medium to strong band in the 1650–1590 cm^{-1} region arises from the NH_2 scissoring vibration. In contrast, NH_3^+ are characterized by N–H bending vibrations in the 1600–1400 cm^{-1} region.

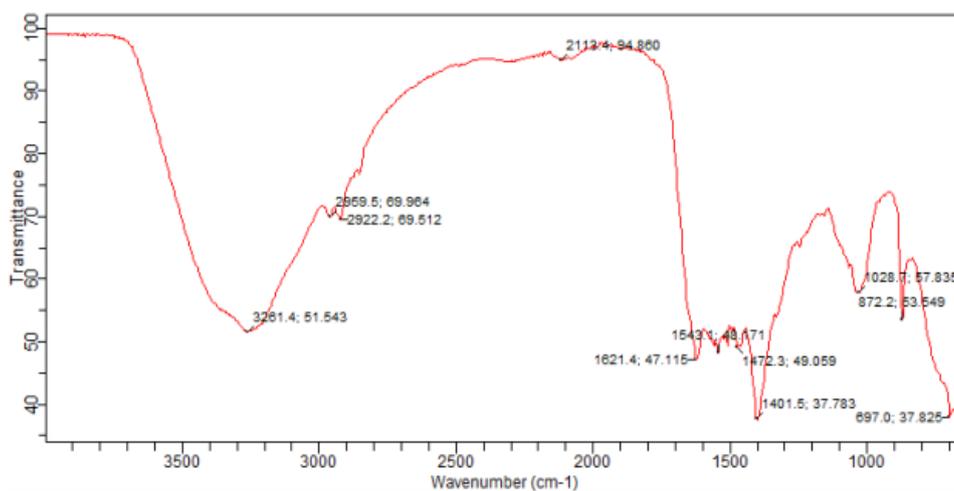


Figure 3.1: FTIR Spectrum of Shrimp shells

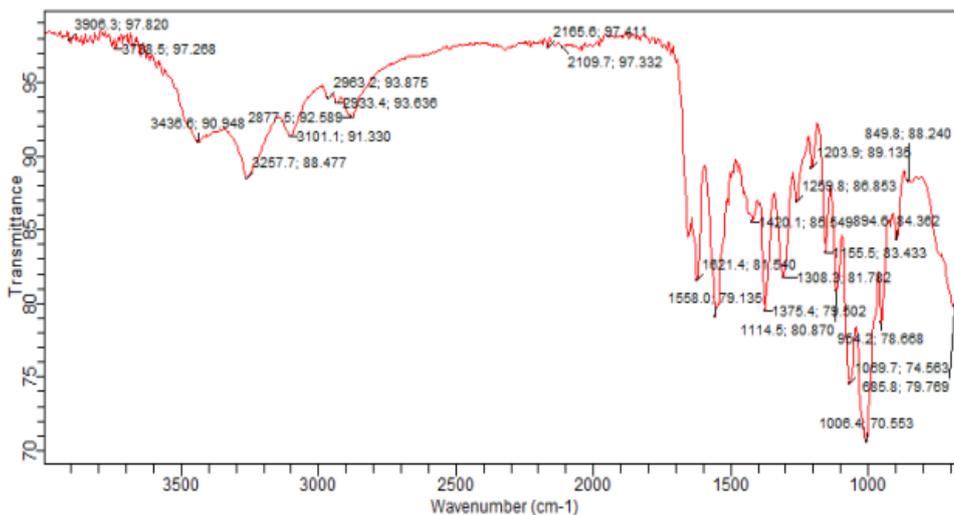


Fig. 3.2: FTIR Spectrum of Crude Chitin

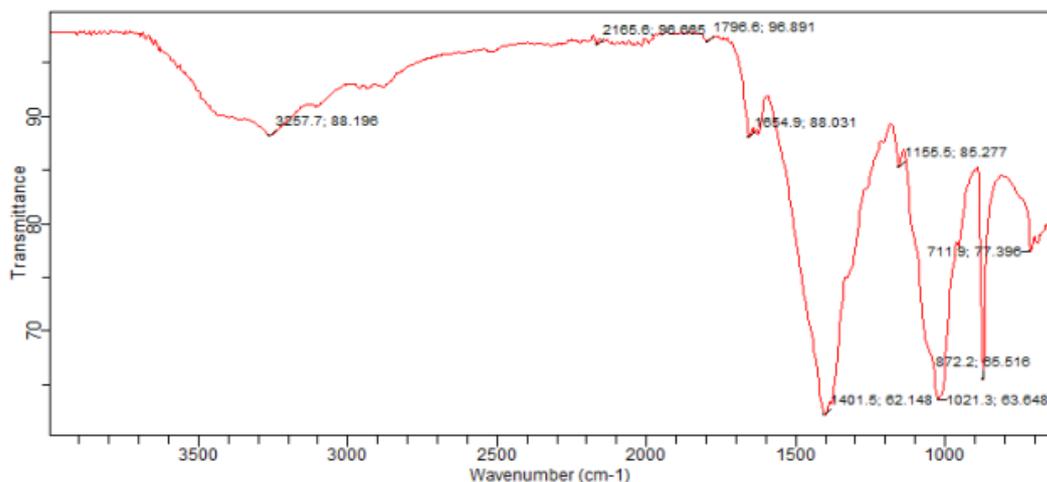


Figure 3.3: FTIR Spectrum of Crude Chitosan

3.4. Coagulation-Flocculation Studies

A number of factors can affect the coagulation–flocculation process. They are: pH, settling time, temperature, coagulant dosage and concentration of the heavy metal ion. These factors individually and collectively have a great influence on the coagulant’s optimum performance. The parameter value that gave the highest of percentage removal was identified as the optimum.

3.4.1. Effect of pH on the coagulation-flocculation of nickel metal ion.

The percentage removal of nickel (II) ions depends greatly on pH as shown in Table 3.3 and Figure 3.4. For the ferric sulphate coagulant, the percentage removal was not gradually increased with increase in pH up to pH 5 with 41.61% value. Afterwards, a steady decrease was observed. However, the crude chitosan had a gradual decrease in percentage removal with pH 3 as optimum (51.29%). In acidic environments, there is competition between hydrogen ions and the metal ions for the negatively charged sites on the coagulant (El-Sayed, Dessouki, Ibrahiem & 2011). The decrease in the percentage removal after pH 3 might also have been caused by the limited ionization of the –COOH groups on the chitosan that limits the bridging actions responsible for the efficient growth of flocs (Mounir, Abdeljalil & Abdallah, 2014).

Table 3.3: Effect of pH on the Coagulation-Flocculation of Nickel Metal Ion.

pH	Percentage Removal, I (%)	
	Ferric Sulphate	Chitosan
3	12.62	51.29
5	41.61	39.18
7	25.95	34.94
9	11.21	23.63
11	5.52	19.19

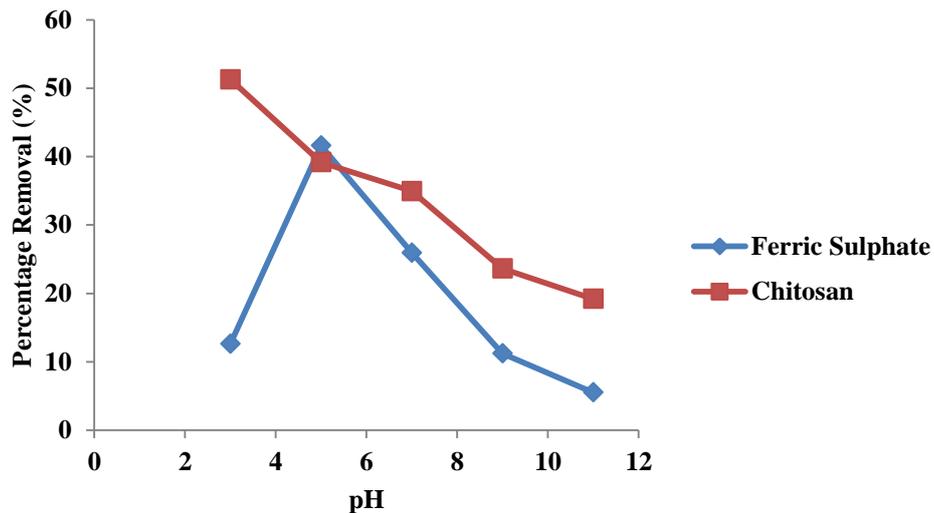


Fig. 3.4: Plot of percentage of nickel metal ion removed at different pH readings.

3.4.2. Effect of Settling Time on the Coagulation-Flocculation of Nickel Metal Ion.

The effect of settling time on the coagulation–flocculation of Ni(II) ions was investigated at optimum pH values of 5 and 3 (for ferric sulphate and chitosan coagulants) respectively. As shown in Table 3.4 and Figure 3.5, the % of Ni(II) removal increased from 41.57% (12mins) upto 52.78% (36mins) for ferric sulphate. On attaining an optimum time of 36 mins, it decreased to 44.10% (60 mins).

For the chitosan coagulant, the optimum time was 48 mins (75.98%). This shows that increase in settling time up to 48 mins favoured the coagulation process using the chitosan coagulant. Prior to attaining their respective optimum settling times, most of the metal ions present in the simulated wastewater solution would interact with the negatively charged sites of the coagulant, facilitating high percentage removal. Progressive occupation of these negatively charged sites after 36 mins (ferric sulphate) and 48 mins (chitosan) resulted to the total available binding sites being limited. A comparable trend has been observed by other researchers (Karthika, Thirunavukkanasu, & Ramesh, 2010; Mishra & Malvika, 2005).

Table 3.4: Effect of Settling Time on the Coagulation-Flocculation of Nickel Metal Ion.

Settling Time (mins)	Percentage Removal, I (%)	
	Ferric Sulphate	Chitosan
12	41.57	51.10
24	43.99	52.22
36	52.78	64.38
48	50.04	75.98
60	44.10	68.82

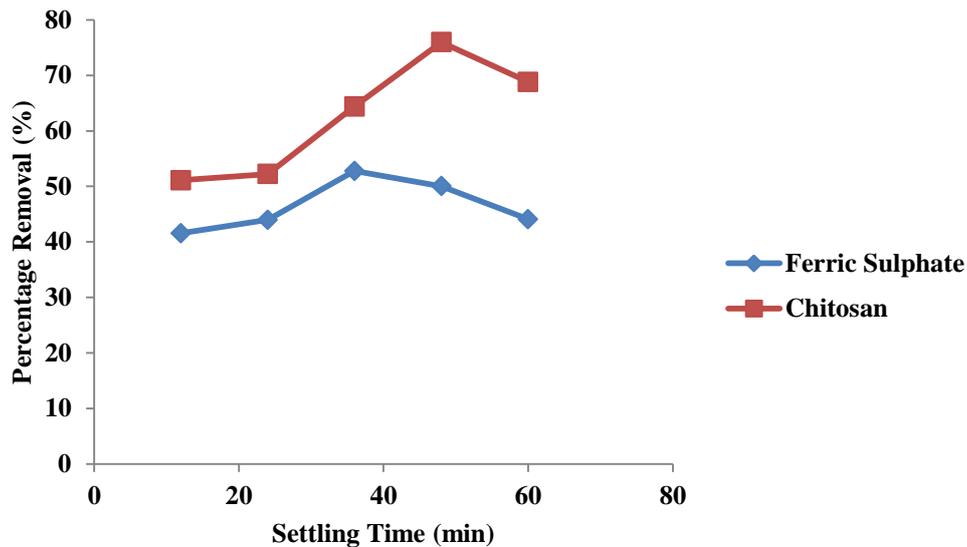


Fig. 3.5: Plot of percentage of nickel metal ion removed at different settling times.

3.4.3. Effect of Temperature on the Coagulation-Flocculation of Nickel Metal Ion.

The effect of temperature on the coagulation/ flocculation of nickel metal ion is represented on Table 3.5 and Figure 3.6 respectively. For the ferric sulphate, with an increase in temperature, the percentage removal of Ni(II) also increased and peaked at 35°C. The optimum values were 67.66% (ferric sulphate at 35°C) and 84.02% (chitosan at 30°C). According to Moss and Dymond, (2015), the flocculation of particles in a liquid depends on collision among particles, caused by their relative motion. The gradual increase in percentage removal of Ni(II) ions between 25 and 35 °C was due to the increase in the diffusion rate of the coagulant throughout the solution. As the viscosity of a fluid increases with decreasing temperature, the poor rapid-mixing conditions caused by low water temperature might lead to inhomogeneous distribution of polyelectrolytes in the water which results in poor coagulation (Duan & Gregory, 2003). Temperatures above the optimum resulted in the rapid movement of particles. The movement disturbed their agglomeration and hence, minimum coagulation–flocculation occurred (Moss & Dymond, 2015).

Table 3.5: Effect of temperature on the coagulation-flocculation of nickel metal ion.

Temperature (°C)	Percentage Removal, I (%)	
	Ferric Sulphate	Chitosan
25	52.63	75.89
30	55.40	84.02
35	67.66	81.62
40	65.70	80.79
45	62.66	77.61

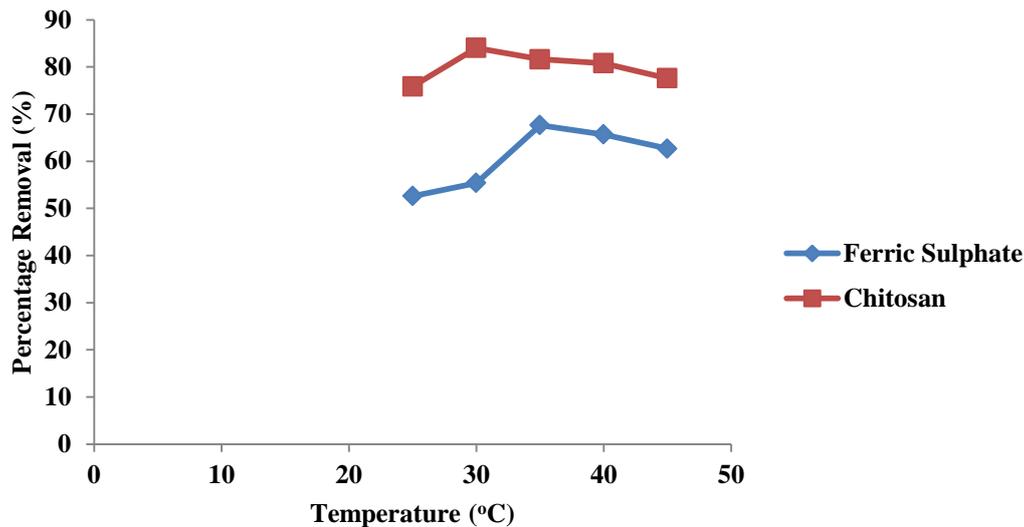


Fig 3.6: Plot of percentage of nickel metal ion removed at different temperatures.

3.4.4. Effect of Coagulant Dosage on the Coagulation-Flocculation of Nickel Metal Ion.

The determination of the optimum coagulant dosage on Ni(II) removal was carried out at optimum pH, optimum settling time and optimum temperature for both coagulants. The dosage was varied in the range of 0.20 to 1.00 g respectively. The Table 3.6 and Figure 3.7 show that the percentage removal of Ni(II) ions increased with increase in coagulant dosages up to the optimum dosage of 0.8g (i.e. ferric sulphate) after which a slight decrease was observed. For the chitosan coagulant, however, there was a steady increase in percentage removal with an increase in coagulant dosage. The increase in the coagulant dosage led to a corresponding increase in negatively charged sites available for Ni(II) aggregation. After the optimum dosage of 0.80g (ferric sulphate), further increase in dosage caused the aggregated particles to re-spread and disturb particle settling. This trend agrees with the findings of other researchers (Bouatay & Mhenni, 2014; Mishra & Malvika, 2005). According to Aygun and Yilmaz, (2010), flocculant usually forms an envelope on the suspended particles and causes them to remain in suspension. Thus, removal efficiency decreases with increasing dosage beyond the optimum. The optimum percentage removal of chitosan coagulant (87.99%) was greater than that of ferric sulphate (74.39%). This shows greater efficiency of the chitosan when compared to the ferric sulphate.

Table 3.6: Effect of coagulant dosage on the coagulation-flocculation of nickel metal ion.

Coagulant Dosage (g)	Percentage Removal, I (%)	
	Ferric Sulphate	Chitosan
0.20	67.82	83.99
0.40	70.66	85.62
0.60	72.07	86.63
0.80	74.39	87.23
1.00	74.22	87.99

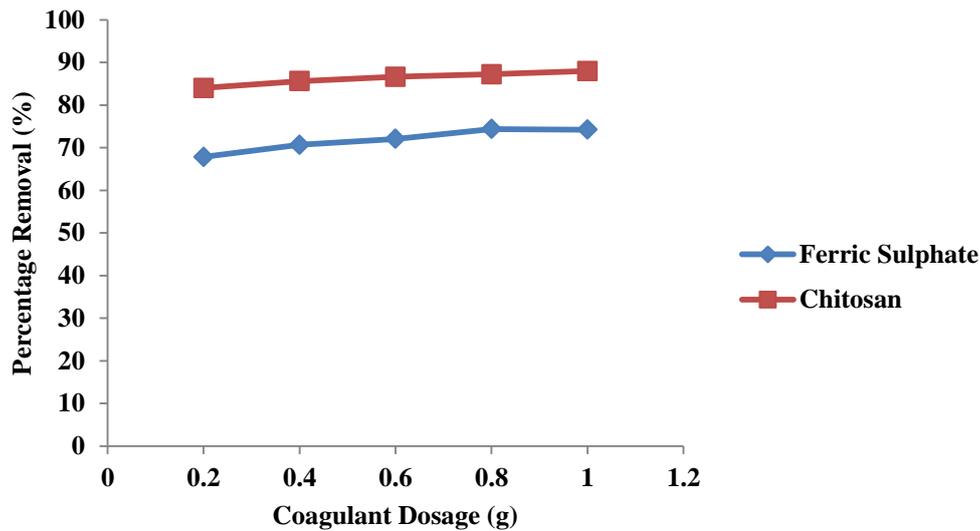


Fig. 3.7: Plot of percentage of nickel metal ion removed at different coagulant dosages.

3.4.5. Effect of Initial Metal Ion Concentration on the Coagulation-Flocculation of Nickel Metal Ion.

The effect of Ni (II) ion concentration on the coagulation behaviour of both ferric sulphate and chitosan was investigated at optimum pH, optimum settling time and optimum temperature respectively. From Table 3.7 and Figure 3.8, the trend shows a decrease in percentage removal of Ni (II) ions with increase in the initial concentration of Ni (II) ions. At lower concentrations of 125mg/L, most of the Ni (II) ions present in the solution would interact with the active sites of the coagulant, resulting in high percentage removal of 74.15% for ferric sulphate and 87.81% for chitosan. At higher concentration of Ni (II) ions, some remained in solution due to the saturation of the negatively charged sites. This led to electrostatic repulsions between the flocculated Ni (II) ions and those in solution. At 225mg/L Ni(II) concentration, the percentage removal further decreased to 56.66% for ferric sulphate and 67.80% for chitosan respectively (Bouatay & Mhenni, 2014; Mahmood, Salman, & Syed, 2010; Mataka, Sajidu, & Mwatseteza, 2010).

Table 3.7: Effect of Initial Metal Ion Concentration on the Coagulation-Flocculation of Nickel Metal Ion.

Initial Metal Ion Concentration (mg/L)	Percentage Removal, I (%)	
	Ferric Sulphate	Chitosan
125	74.15	87.81
150	61.04	78.16
175	60.46	72.05
200	58.47	70.00
225	56.66	67.80

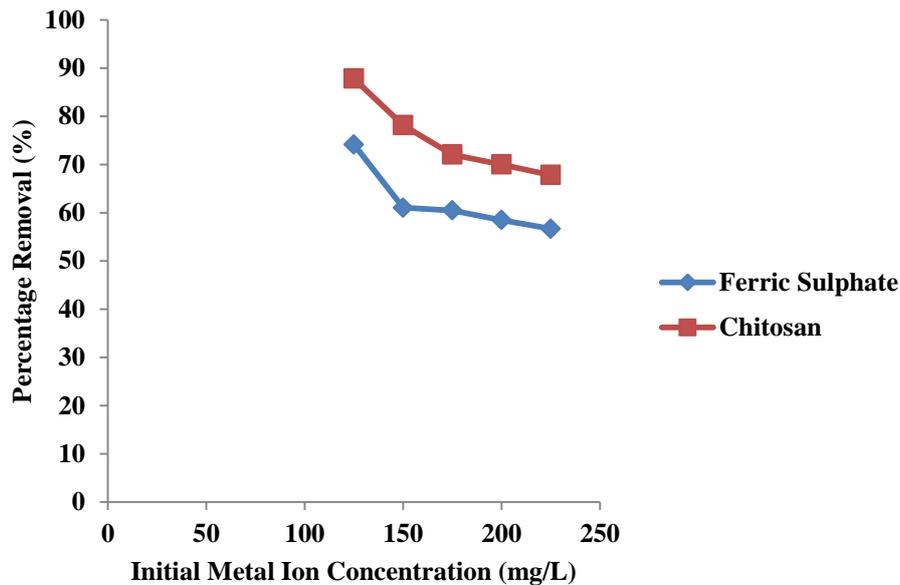


Figure 3.8: Plot of percentage of nickel metal ion removed at different metal ion concentrations.

4. Conclusion

This study attempted to compare the performances of ferric sulphate and chitosan as coagulants in the treatment of nickel contaminated wastewater. Both ferric sulphate and chitosan are good coagulants for nickel contaminated wastewater. Distinct decrease of the nickel concentrations (increased removal efficiencies) during the coagulation-flocculation process was observed implying their removal from the wastewater. Chitosan, however, performed better than the ferric sulphate during the treatment processes. As such, it is always prudent for water treatment practitioners to cautiously select the most suitable coagulant for better treatment results.

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References

- Abdou, E.S., Nagy K.S.A. & Elsabee, M.Z. (2008). Extraction and characterization of chitin and chitosan from local sources. *Bioresources Technology*, 99, 1359-1367.
- Abdulwadud A., Muhammed T. I., Surajudeen A., Abubakar J. M. & Alewo O. A. (2013). Extraction and Characterisation of Chitin and Chitosan from Mussel Shell, *Civil and Environmental Research*, 3 (2), 2222-2863.
- Abia, A.A., Harsfall, M. & Didi, O. (2003). The use of chemically modified and unmodified cassava waste for the removal of Cd, Cu and Zn ions from aqueous solution. *Bioresour Technol*, 90(3), 345-348.

- Armenante, P.M. (2014). Coagulation and flocculation. Retrived from cpe.njit.edu/dlnotes/che685/cls07-1.pdf.
- Aygun, A.& Yilmaz, T. (2010). Improvement of coagulation–flocculation process for treatment of detergent wastewaters using coagulant aids. *International Journal of Chemical and Environmental Engineering*, 1(2), 98–101.
- Bolto, B. & Gregory, J. (2007). Water research: Organic polyelectrolytes in water treatment. *Journal of Environmental Science*, 41, 2301-2324.
- Bouatay, F. & Mhenni, F. (2014). Use of the cactus cladodes mucilage (*Opuntia Ficus Indica*) as an eco-friendly flocculant: Process development and optimization using statistical analysis. *International Journal of Environmental Resources*, 8(4), 1295–1308.
- Brugnerotto, J., Lizardi, J., Goycoolea, F.M., Arguelles-Monal, W., Desbrieres, J.&Rinaudo, M., (2001). An infrared investigation in relation with chitin and chitosan characterization. *Journal of Polymer Science*, 42, 3559–80.
- Carpinteyro-Urban, S.& Torres, L.G. (2013). Use of response surface methodology in the optimization of coagulation–flocculation of wastewaters employing biopolymers. *International Journal of Environmental Resources*, 7(3), 717–726.
- Chukwudi, B.C.& Uche, R. (2008). Flocculation of kaolinite clay using natural polymer. *Journal of Science and Technology*, 9(2), 495–501.
- Duan, J.& Gregory, J., (2003). Coagulation by hydrolyzing metal salts. *Advanced Colloid Interface Science*, 100–102, 475–502.
- Duruibe, J. O., Ogwuegbu, M.& Ekwurugwu, J. N. (2007). Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences*, 2(5), 112-118.
- El-Sayed, G.O., Dessouki, H.A. & Ibrahim, S.S. (2011). Removal of Zn (II), Cd (II) and Mn(II) from aqueous solution by adsorption on maize stalks. *Malaysian Journal of Analytical Science*, 15(1), 8–21.
- Fernandez, L. G.& Olalla, H. Y. (2000). Toxicity and bioaccumulation of lead and cadmium in marine protozoan communities. *Ecotoxicology and Environmental Safety Journal*, 47, 36-41.
- Gardea-Torresdey, J. I., Peratta-Videa, J. R., Rosa, G. D.& Parson, J. G. (2005). Phytoremediation of heavy metals and study of the metal coordination by X-ray absorption spectroscopy. *International Journal of Applied Science*, 249(17-18), 1797-1810.
- Islam, M.M., Masum, S.M., Molla, M.A.I., Rahman, M.M., Shaikh, A.A. & Roy, S.K. (2011). Preparation of Chitosan from Shrimp Shell. *International Journal of Basic & Applied Sciences*, 11(1), 116-130.
- Jern, W. (2006). Industrial wastewater treatment. *Singapore: Imperial College Press*.
- Kalut, S.A. (2008). Enhancement of degree of deacetylation of chitin in chitosan production. *B. Chemical Engineering, University Malaysia Pahang*, 2.
- Karthika, K., Thirunavukkanasu, A. & Ramesh, S. (2010). Biosorption of copper from aqueous solution using *Tridax procumbens*. *Journal of Science and Technology*, 2(3), 86–91.
- Khanafari, A., Marandi, R & Sanatei, S. (2008). Recovery of chitin and chitosan from shrimp waste by chemical and microbial method. *Iran. Journal of Environmental Health Science and Engineering*, 5(1), 19-24.
- Kumar, M.N.V.R. (2000). A review of chitin and chitosan applications. *Journal of Polymer Science.*, 46, 1-27.

- Li, Z., Li, N., Zhang, H. & Liu, D. (2009) Studies and application processes on flocculant in water treatment in China. *International Journal of Biological Macromolecules*, 14, 134–138.
- Mahmood, T., Salman, A.M. & Syed, T.H. (2010). Biosorption and recovery of heavy metals from aqueous solutions by water hyacinth ash. *BioResources*, 52(2), 1244–1256.
- Marguerite, R., (2006). Chitin and chitosan: Properties and applications; *Progress Polymer Science*. 31, 603–632.
- Mataka, L.M., Sajidu, S.M.I. & Mwatseteza, J.F., (2010). Cadmium sorption by *Moringa stenopetala* and *Moringa oleifera* seed powders: batch, time, temperature, pH and adsorption isotherm studies. *International Journal of Water Resources and Environmental Engineering*, 2(3), 55–67.
- Mishra A. & Malvika, B., (2005). Flocculation behavior of model textile waste water treated with a food grade polysaccharide. *Journal of Hazardous Materials*, 118 (1–3), 213–217.
- Moss, N. & Dymond, B. (2015). Flocculation: theory and application. Retrieved from www.siltstop.com/pdf/flocculation-theory_application.pdf.
- Mounir, B., Abdeljalil, Z. & Abdellah, A. (2014). Comparison of the efficacy of two Bio-flocculants in water treatment. *International Journal of Science and Engineering Technology*, 3(6), 734–737.
- Muhammed T. I., Alewo O. A., Joseph O. G. & Kenneth K. A., (2012). Extraction and Characterization of Chitin from Nigerian Sources. *Leonardo Electronic Journal of Practices and Technologies*, 2, 73–81.
- Muzzarelli, R.A.A., (1997). Some modified chitosan and their niche applications. *Chitin Handbook*, Muzzarelli RAA, Peter MG (eds). *European Chitin Society Italy*, 47-52.
- Ogoyi, D. O., Mwita, C. J., Nguu, E. K. & Shiundu, P. M. (2011). Determination of heavy metal content in water, sediment and microalgae from lake victoria, East Africa. *The Open Environmental Journal*, 4, 156-161.
- Salem, H. M., Eweida, E. A. & Farag, A. (2000). Heavy metals in drinking water and their environmental impact on human health. *Greener Journal of Environmental Management and Public Safety*, 2(4), 172-179.
- Shigemasa, Y., Matsuura, H., Sashiwa, H. & Saimoto, H. (2006). Heavy metal contamination. *International Journal of Biological Macromolecules*, 18, 237.
- Srivastava, N. K. & Majumder, C. B. (2008). Novel biofiltration methods for the treatment of heavy metals from industrial wastewater. *Journal of Hazardous Materials*, 151, 1-8.
- Varma, A. J., Deshpande, S. V. & Kennedy, J. F. (2004). Metal complexation by chitosan and its derivatives: A review. *Carbohydrate Polymers*, 55(1), 77-93.
- Varsha, P. & Jay, P. (2012) Mucilage extract of *Cocinia indica* fruit as coagulant–flocculant for turbidity water treatment. *Asian Journal Plant Science Res*, 2(4), 442–445.