

«Original Articles »

Efficiency evaluation of Zinc and Nickel removal through coagulation and flocculation process using chitosan

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Abstract

Background: The release of large quantities of zinc(Zn) and nickel(Ni) into the natural environment cause some environmental problems. The aim of this research was investigation the effect of chitosan biopolymer as a natural fluctuant in order to remove Zn^{2+} and Ni^{2+} from aqueous solutions.

Material and methods: Experiment in batch system as the half experiment study with change in effective parameters such as pH (6-9), dose of coagulant (10-100 mg/l), settling time and initial amount of metal was investigated.

Results: Results of this study showed that Zn^{2+} and Ni^{2+} removal increases with pH increases. The optimal amount of coagulant used for this study was defined between 60 - 100 mg / l respectively. So the results of this study also showed that initial concentration of metal had inverse relation with Zn and Ni removal efficiencies in coagulation and flocculation processes.

Conclusion: Due to chitosan properties such as biocompatibility, biodegradability, ability to remove heavy metals and also having amine, hydroxyl and carboxylic function groups it can be use as a coagulant and/or flocculant to remove heavy metals from aqueous solutions.

Keywords: chitosan, coagulation and flocculation, zinc, nickel

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Introduction

Increasing application of metals and chemical materials in industrial process has been resulted in production of massive effluents with huge amounts of toxic heavy metals. Due to increasing amounts of discharge and presence of these pollutants (heavy metals) which are toxic and have other negative effects on receptive waters in environment, has created great concerns. Unlike the organic compounds, these pollutants are non-degradable and tend to bio-accumulation in living organisms (1). Zn and Ni are among these metals which are used most often in industries to produce stainless steel, metallic alloys, chargeable batteries, catalyzers, coins, casting and metallurgy. They are entered into environment through natural ways and human activities and cause pollution in environment (2, 3).

Zn and Ni in trace concentrations are among necessary elements and function as micronutrients in body. Also these two elements are very important in physiological activities of living tissues and controlling biochemical processes. However, in high concentration they cause problems for human such as stomach pain, skin burn, vomiting and nausea, anemia, cancer, cardiopulmonary disorders, asthma, chronic bronchitis, brain damage and etc. Due to health concerns and potential toxicity and also increasing exposure of humans by Zn and Ni, several organizations have recommended guidelines including MCL for these two metals for drinking water. For example, WHO standards for Zn and Ni in drinking water are 0.02 and 3 mg/L, respectively (2, 4- 6).

Conventional treatment methods for removing Zn and Ni from polluted water include chemical precipitation, ion exchange, activated carbon absorption, membrane processes (RO and electro dialyze) and biosorption. Because these methods have their own disadvantages such as high expenses for maintenance and operation and machinery, massive

production of sludge and other toxic wastes, and need for high energy consumption and need for pre-treatment process-production. Among above mentioned methods, Zn and Ni Absorption on flocks of Fe and Al saline's and simple precipitation are more common due to simplicity and effectiveness (7- 10). During flocculation and coagulation process, colloid particles become unstable by adding chemical coagulants and then attached together and produce settleable and larger particles. However, despite the relatively high efficiency of chemical coagulants (such as Alum and poly aluminum chloride) they are rather expensive and may pose adverse impacts on human health in long-term periods and produce massive bulks of sludge. So, using natural materials may reduce related expenses for chemical coagulant supply such as alum powder. For this reason, in recent years application of natural organic polymers such as chitosan has been increased (11, 12).

Chitosan is one of cationic poly electrolytes which is derived from chitin with chemical name β -D (1-4) N-acetyl-glucosamine and is named poly(B-(1,4)-2-anaino-2-deoxy-D-glucose) and is the most abundant natural polymer after cellulose (figure 1). This material is found in crustacean, insects and cellular wall cell of fungi. Chitosan is a natural and linear hetero poly-saccharide with high molecular weight and has other characteristics such as being soluble in different mediums, degradable, hydrophilic, biocompatible, antibacterial, and anti-oxidant, and agent for removing metals. This biopolymer is poly cationic at PH values under 6 and simply reacts with compound with negative charge such as anionic poly saccharides, fatty acids, and phospholipids. Chitosan performs coagulation and flocculation through charge neutralization, adsorption and interparticle bridging (13- 19).

Most recent researches have shown that Chitosan has been effective as a coagulant

or absorbent for removing heavy metals and colloid particles. Hassan et al, used it as coagulant to remove turbidity and COD. Obtained results showed that remove ratio (at PH =4) for turbidity is 94.9% and for COD 72.5 % (20). Guibal and Roussy (2007) investigated coagulation of color solutions by Chitosan and results showed that at PH values equal 3, less Chitosan is needed to remove colors (16). In another research, Juang and Shao have removed Zn and Ni and Cu from aquatic solutions by Chitosan. They found that absorption of metals by Chitosan is highly related with PH values (14). Bratskaya et al, in their research found that removal ratio for metals is promoted as PH values and coagulant dosage were increased (21). Bamgbose et al (2010) evaluated absorption of Cd and Pb by Chitosan and found that absorption process is highly related with Freundlich isotherm and also the metal removal ratio has direct relationship with initial concentration (22). Regarding mentioned researches and importance of known impacts related to Zn and Ni exposure by water and also scarcity of studies about application of Chitosan as coagulant to remove Zn and Ni, the aim of this study is evaluation of Chitosan efficiency as coagulant for Zn and Ni removal together with investigation of variables such as PH values, consumed coagulant dosage, settling time and concentration of Zn and Ni.

Material and methods

Survey of method

This interventional semi-experimental research was performed on prepared synthetic samples in Jondishapoor Ahvaz University.

Materials and reagents

1000 ml stock solution of Ni^{2+} and Zn^{2+} was provided using dissolving $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and ZnCl_2 in distilled water. All chemical materials used in this research was provided from, Merck corporation in Germany.

Providing chitosan stock solution

Chitosan powder was provided from Sigma Chemical Company with diacetylation degree of 75%-85% with average molecular weight. To provide chitosan 500 ppm stock solution, 100 mg chitosan was dissolved in 0.5 ml HCl (2mollar) and 9.5ml distilled water and then 190 ml distilled water was added obtained solution (23).

Jar test

Jar test was done in 6 jars (1 liter volume). In each jar, 1 liter sample containing Zn and Ni (25 mg/L) and then chitosan (25 mg/L) were added. In this research, the effect of pH and chitosan dosage (as coagulant) was investigated on removing Zn and Ni in flocculation and coagulation process. To determine optimum pH value, jar test was done with samples at different pH values between 6 to 9. After determining optimum PH, to obtain optimum chitosan concentration for Zn and Ni removal, different chitosan concentrations (between 10 and 100mg/L) were added to jars. For each variable jar test was done separately.

Jar test was done with 120 Rpm (round per minute) for rapid mixing and 30 Rpm for flocculation process and 30 minutes settling time for Zn and Ni removal. After settling time, samples were taken from 5 Cm depth under water surface. Then samples were filtered using filter paper and Zn and Ni concentrations were determined by flame atomic absorption (AAS 5FL model- made in Germany). The sample with least Zn and Ni concentration was considered as optimum PH and coagulant value for Zn and Ni removal. All these tests were repeated 2 times and variables were evaluated during 2 phases.

Results

The obtained results indicated that as pH values increased from 6 to 9, the percentage of Zn and Ni removal were increased from 10.1% and 3.4% to 81.8% and 51.08%, respectively (figure 2). Also by increasing coagulant dosage from 10 to

100 mg/L, the percentage of Zn and Ni removal were increased from 75% and 40.8 % to 98.5.8% and 87.9%, respectively (figure 3). To evaluate efficiency of settling time Zn and Ni removal, settling times between 30 and 240 minutes were tested. As figure 4 indicates, Zn and Ni removal increases as settling time raises. To evaluate the effect of initial metal concentration on process efficiency, Zn and Ni concentrations equal to 3, 5, 10, 50

and 100 mg/L were used. Obtained results showed that Zn and Ni removal were decreased as initial metal concentration were increased, so that in low metal concentration, the efficiency of process is higher. For example, as Zn and Ni concentrations increase from 10 mg/L to 100 mg/,the Process efficiency decreases from 98% to 89%. Figure 5 shows the effect of different Zn and Ni concentrations on process efficiency.

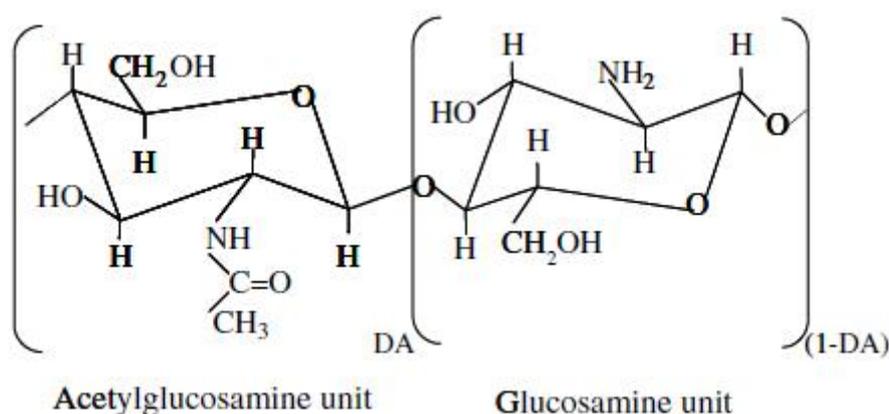


Fig.1: Structure of chitosan (DA: degree of acetylation) (16)

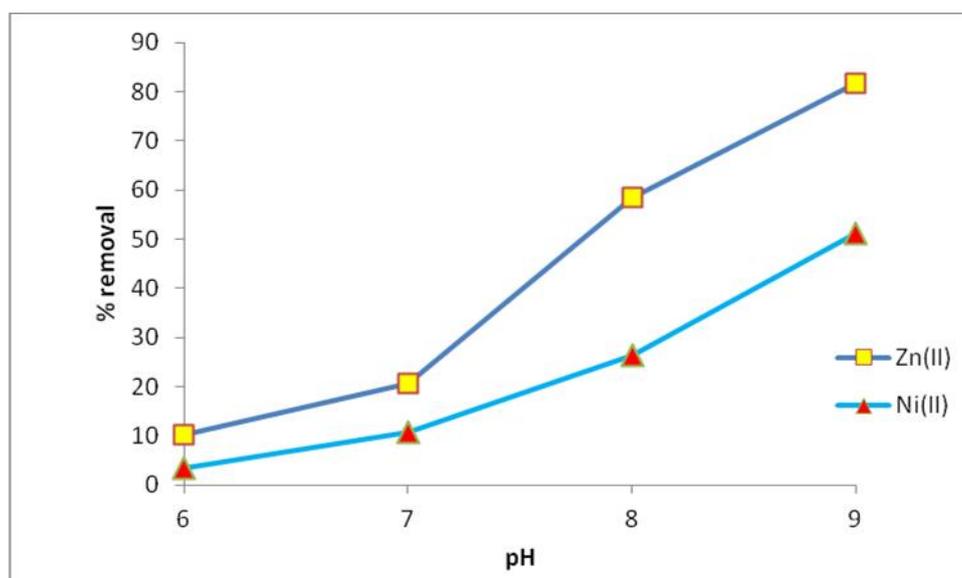


fig.2: Effect of pH on Zn and Ni removal (Zn=25mg/L, Ni=25mg/L, settling time=30 min)

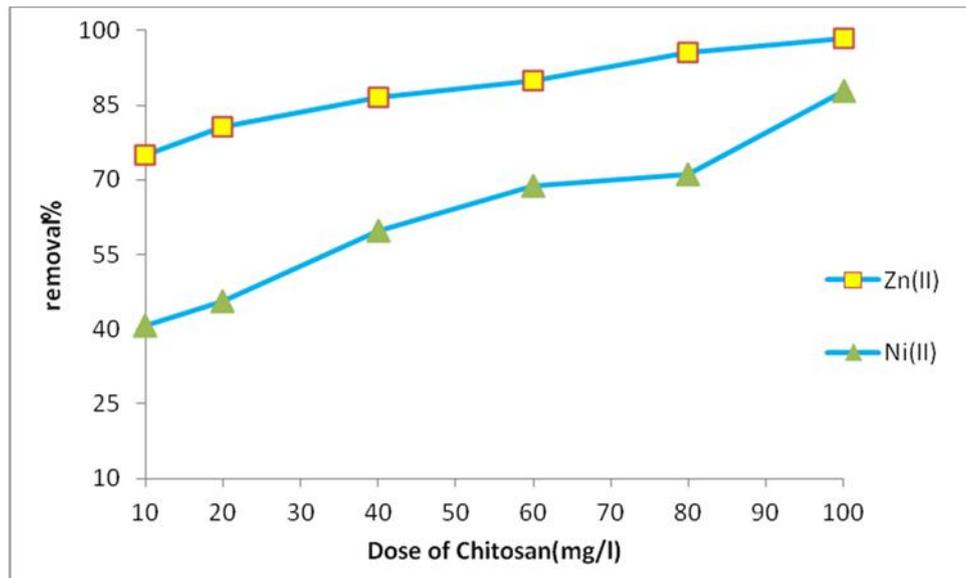


fig. 3: Effect of chitosan concentration on Zn and Ni removal (Zn=25mg/L, Ni=25mg/L, settling time=30 min)

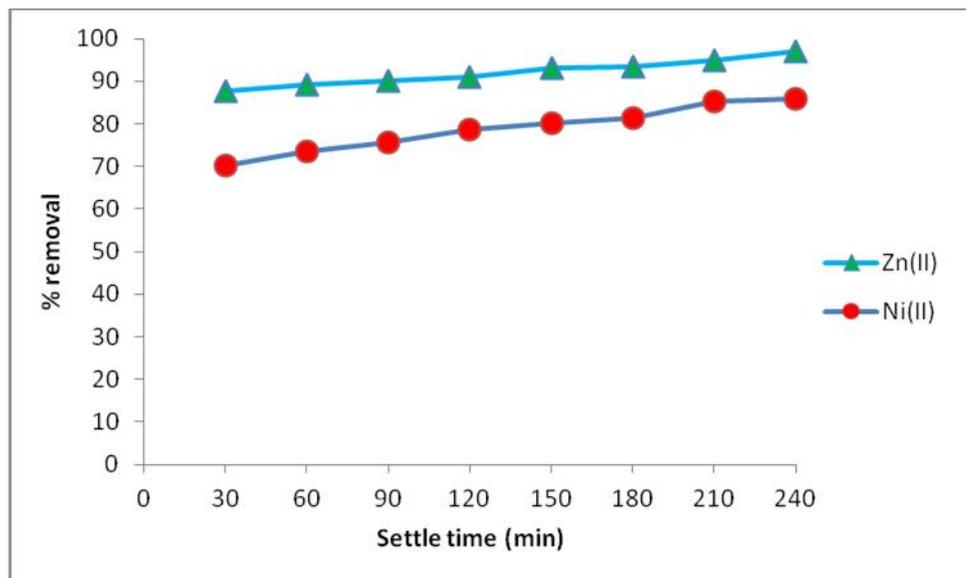


fig. 4: Effect of settle time on Zn and Ni removal (Zn=25mg/L, Ni=25mg/L, pH=9)

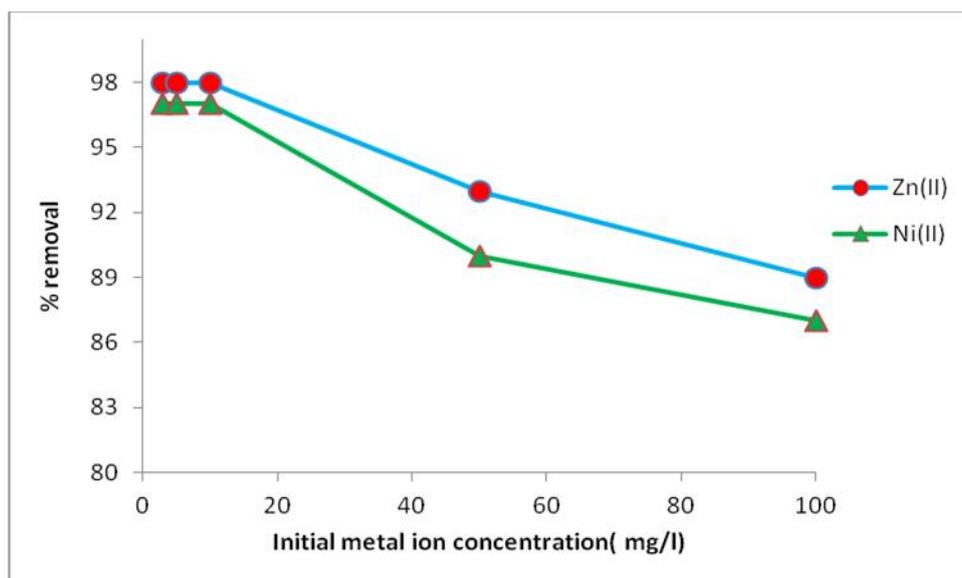


fig. 5: Effect of initial metal concentration on Zn and Ni removal (Zn=25mg/L, Ni=25mg/L, pH=9, settle time=30min)

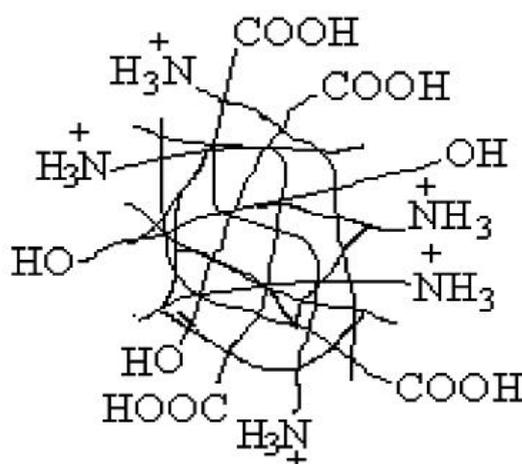


Fig. 6: The chemical nature of chitosan at low pH (32)

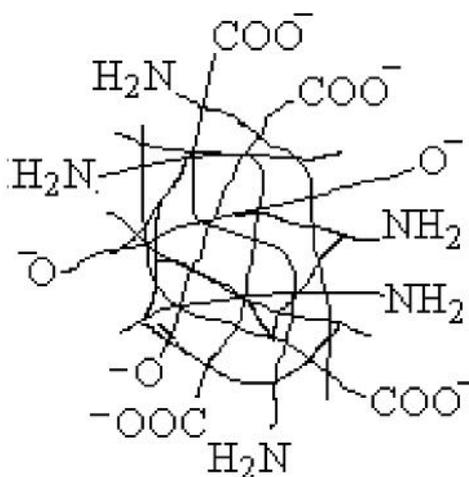


Fig. 7: The chemical nature of chitosan at high pH(32)

Discussion

Zn and Ni removal from aqua environments using chitosan biopolymer is under effect of pH values, because pH is among the critical parameters in efficiency of coagulation and flocculation process. This parameter is effective on solution characteristics, biopolymer behavior in solution and stability of suspension and is one of the key variables in coagulation and flocculation process (20). In addition to pH, also pK_a is among the critical parameters for chitosan (as coagulant) because chitosan receives electrical charge (like other protein compounds) due to ionization of groups such as ($-NH_2$) and ($-COOH$) which have located on surface. When pH reaches at isoelectric point, the total or net electrical charge is zero, because amino groups ($-NH_3^+$) and carboxyl group (COO^-) is being ionized. In pH values less than isoelectric point, carboxyl group ($-COOH$) is not ionized and chitosan get positive electrical charge due to amino groups (figure 6). At pH values higher than isoelectric point, amino group losses one hydrogen and produce a neutral group ($-NH_2$) and chitosan get negative charge due to carboxyl group (figure 7). For this reason, when chitosan has positive charge ($pH > pK_a$) is simply reacts with compounds with negative charge (such as proteins, anionic polysaccharides, fatty acids, metal compounds with negative charge) and when gets positive charge ($pK_a > pH$) it reacts with positive charge compounds (24). In this study, the isoelectric point of chitosan is equal to 6.8.

Figure 2 shows that the more pH value increases, the more Zn and Ni removal ratio. This increase trend for Zn and Ni removal is further continues due to reduction in distribution of cationic sites of amino groups and also increase for negative charge (through ionization of carboxyl groups with negative charge) (21). According to Figure 2, the highest Zn and Ni removal ratio is occurred at $pH=9$,

so the optimum pH value was determined as $pH=9$. Because pK_a value for used chitosan is equal to 6.8, the increase for efficiency of Zn and Ni removal in alkaline conditions is logical due to increase for negative charge of chitosan and cationic property of these two metals. Obtained results were in comparison with Brateskaya et al (21).

Figure 3 shows the increase for Zn and Ni removal as chitosan dosage increases. According to this figure, the most removal for Zn and Ni occurs at coagulant dosage equal to 100 mg/L. so; the optimum dosage concentration was determined to be equal to 100 mg/L. This increase for Zn and Ni removal is related to Amino-groups deprotonated and also increase for negative charge (due to ionization of carboxylic group) at optimum PH point for Ni and Zn removal. At $pH=9$ (optimum PH), amino groups are in the form of deprotonated and carboxylic groups cause to metal removal through chelate mechanism and charge neutralization and interparticle bridging (19-21,25, 26). Furthermore, these results can be defined on the basis of charge density. Chitosan has more charge density comparing other coagulants. Also the removal ratio for Zn and Ni by polymer increases due to polymer charge density. So, as chitosan increases, significant amounts of Zn and Ni are removed from aquatic solutions (27-28). Bratskaya et al (2009) performed a study titled "metal removal by N-2-carboxyl ethyl-chitosan". Related results showed that removal for Ni and Zn and Cu increases as chitosan dosage raises (21).

To evaluate the effect of settling time on efficiency of Zn and Ni removal by chitosan, the tests were done at stable conditions ($pH=11$ and initial metal concentration equal to 25 mg/L). Related results were shown in figure 4. As figure 4 shows, as settling time increase, the removal efficiency is improved. This improvement is related to more flocks

which are created by chitosan, as time passes. In our study, the maximum removal ratio obtained with settling time equal to 240 minutes. But removal efficiency for this settling time is has not significant difference with settling time equal to 30 minutes. So, in this study, due to cost reduction, the optimum settling time for Zn and Ni removal was considered to be 30 minutes. In research which was done by Ahmad et al (2008) and titled suspended particles coagulation and flocculation by PAC, alum and chitosan it was recognized that chitosan has the highest removal efficiency at low settling time (30 minutes) for suspended particles (27). Also in researches which were conducted by Chi and Chang (2006) it was discovered that chitosan has the best efficiency ratio for dairy effluent treatment with 30 minutes settling time (29).

The effect of initial metal concentration on Zn and Ni removal by chitosan in constant conditions was evaluated. The obtained results were summarized in figure 5 .According to this figure, initial metal concentration has reverse effect on Zn and Ni removal ratio, so that removal ratio increases as initial metal concentration is reduced and vice versa. This reduction in Zn and Ni removal in high concentrations may be explained that the more initial Zn and Ni concentration, the less absorption ratio and neutralization and interparticle bridging .Our results is similar to results which obtained by Bojic et al and Xu et al (30,31).

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In Conclusion In present study, coagulation and flocculation by chitosan to remove Zn and Ni metals from aquatic solutions was evaluated. The removal ratio for Zn and Ni in different PH values, coagulant dosages, settling times and initial metal concentrations were evaluated. Obtained results showed that:

1-Zn and Ni removal by chitosan is increased as pH value rises. This increase is caused due deprotonization of Amino groups at high pH values and dominance of mechanisms including adsorption and interparticle bridging and charge neutralization.

2-Zn and Ni removal by chitosan is increased as initial chitosan dosage is increased. This improve is related to increase for deprotonated amino-groups and surface charge of chitosan.

3-The efficiency of Zn and Ni removal by chitosan is increased as settling time is raised. This increase is attributed to more floc formation by usage of chitosan biopolymer, as time passes.

4-The efficiency of Zn and Ni removal by chitosan is decreased if initial concentration of Zn and Ni is increased. This is because the coagulant dosage is not enough and adsorption surface is decreased.

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