

original article

Removal of zinc and nickel from aqueous solution by chitosan and polyaluminum chloride

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INTRODUCTION

The release of large amounts of heavy metals into the natural environment has resulted in a number of ecological and health problems. Many industrial processes such as metal finishing, electroplating, nonferrous metal works, paper, and petroleum produce wastewater flows containing heavy metals which are toxic to nature. Such toxic metals can be presented in the other environments since they are not biodegradable

and can be accumulated in living organisms. Some metals, such as zinc (Zn) and iron, are regarded bioessential while others such as cadmium, mercury, and chromium are highly toxic. However, even bioessential metals may cause health and ecological problems if present at a considerable amount. Two metal ions which are often released into nature through

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ABSTRACT

Aims: The purpose of this study is to investigate the zinc (Zn) and nickel (Ni) removal from aqueous solution by coagulation–flocculation using polyaluminum chloride (PACl) and chitosan (CS) biopolymer.

Materials and Methods: This study was a laboratory scale experiment, which used PACl and CS to remove Zn and Ni with concentrations 3–100 mg/L from aqueous solutions. Jar test was used to compare the Zn and Ni removal efficiencies of the chemical treatment options using PACl and CS. The dosages used for PACl ranged from 5 to 100 mg/L whereas CS dosages varied between 5 and 75 mg/L.

Results: The results showed that optimum coagulant doses and pH were found at 50–100 mg/L and 11 for PACl and 20–75 mg/L and 11 for CS, respectively, when CS added with PACl led to a better removal efficiency of the metals (more of 99%). In mixed aqueous solution, the presence of Zn caused increase of Ni removal efficiency and the presence of Ni caused decrease of Zn removal efficacy.

Conclusion: The results of this study showed that CS had higher removal efficiency than PACl for removal of Zn and Ni, and also CS as a coagulant aid led to increasing in metal removal.

Key words: Chitosan, coagulation–flocculation, heavy metal, polyaluminum chloride

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industrial activities at concentrations of health and ecological concern are Zn and Ni.^[1-5]

Zn is a trace element that is essential for life and acts as a micronutrient when presents in trace amounts. It is important for the physiological functions of living tissue and controls many biochemical processes. However, too large amount of Zn can cause prominent health problems, such as muscular stiffness, loss of appetite, stomach cramps, skin irritations, vomiting, nausea, and anemia.^[3,6,7] The Ni ion, compared to other heavy metals, is a more rebellious pollutant. The effects of Ni exposure vary from skin irritation to damage to the lungs, nervous system, and mucous membranes as chest pain, tightness of the chest, and dry cough, respectively.^[2,8,9] Taking according to its health effects and toxicology, occurrence and human exposure, different regulatory agencies have recommended a maximum contaminant level for heavy metal in drinking water, e.g., the current WHO guideline value for Ni (II) and Zn (II) in drinking water is 0.02 and 3 mg/L, respectively. Therefore, the removal of excess Ni and Zn ions from wastewater is essential.^[10]

Conventional technologies have been employed for the removal of heavy metal including chemical precipitation, electrocoagulation, adsorption, electrolysis, ion exchange, and reverse osmosis.^[6,11-14] However, these methods require high capital investment as well as creating sludge disposal difficulty.^[15] Coagulation is very much the most widely used process to remove the heavy metal in water.^[6] Recent studies have indicated that heavy metal in wastewater is removed by coagulation with iron- or aluminum-based coagulant.^[16-19] Coagulation is a kind of physicochemical technique which uses metal oxide or metal hydroxide (ferry, aluminum, and calcium) for destabilizing and collecting colloids or coagulates heavy metal. There are number of different mechanisms involved in a coagulation process, including coherence and enmeshment, adsorption and charge neutralization, interparticle bridging, and sweep coagulation. These mechanisms are very important in forming flocs of heavy metal and suspended solid which could be easily settled and finally removed. The most common coagulants used are aluminum and iron salts, such as aluminum sulfate (generally known as alum) and ferric chloride.^[20-23] More recently, new generation of coagulants–inorganic polymer flocculants (IPFs) due to advantages such as positively charged monomers and polymers, formation of rapid and denser floc, and reduced sludge has been becoming more and more popular.^[24,25] One of the major IPFs, polyaluminum chloride (PACI), is made by fragmentary hydrolysis of acid aluminum chloride solution using a specific reactor and used extensively for water and wastewater treatment. PACI contains different amounts of hydroxyl, and the molecular formula of PACI is $[Al_m(OH)_n(H_2O)_x].Cl_{3m-n}$ ($n \leq 3$ m).^[26,27] However, the use of some conventional materials for coagulation and flocculation is frequently discussed due to causes of environmental problems such as aggregation in the food chain, Alzheimer disease, and produce material toxic by-products.^[26-29]

For these reasons, in recent years, there has been considerable interest in the advancement of natural coagulants.^[30] Natural coagulants extracted from waste can serve as alternatives to synthetic polyelectrolyte because they are biodegradable, renewable, produce no secondary pollution, cost-effective aspects, are safe for human health, and have a wider effective dosage range for flocculation of colloidal suspension.^[29,31] Among these natural products, chitosan (CS) has received a great amount of attention for the past 20 years for many applications in wastewater treatment.^[32]

CS is a linear cationic polymer of D-glucosamine and N-acetyl-D-glucosamine produced by deacetylation of chitin (poly-N-acetyl glucosamine), the second most abundant natural organic resource only next to cellulose on the earth. Chitin and its derivative (CS) are manufactured from the outer shell of crustaceans (such as crabs, shrimps, prawns, and lobsters), fungi, and yeast. CS possesses several intrinsic properties such as its nontoxicity, inexpensive, biodegradability, biocompatibility, and its outstanding chelating behavior that make it an effective coagulant and/or flocculants for the removal of contaminants in the dissolved state. It has characteristics of both coagulants and flocculants, i.e., high cationic charge density, long polymer chains, bridging of aggregates, and precipitation (in neutral or alkaline pH conditions). Furthermore, the physicochemical properties of CS related to the presence of amine and carboxylic functions make it very efficient for coagulation and binding metal cations in alkali and neutral solutions and for interacting with anionic solutes in acidic solutions.^[33-38]

The main objective of this study was to investigate Zn and Ni removal by PACI in conjunction with CS from aqueous solutions. The effect of pH, type, and dosage of coagulant on metal removal and effect of amount of coagulant aid on the Zn and Ni were studied.

MATERIALS AND METHODS

Chemicals and reagents

Analytical grade reagents were used in experimental studies. Chloride salts of test metals (ZnCl₂ and NiCl₂·6H₂O from Merck) were used for preparing certain concentrations of synthetic solutions. Polysaccharide CS (CS, 75–85% deacetylation) and PACI were purchased from sigma chemical. Deionized water was used to prepare all stock solutions. The pH adjustments were carried out using 0.1N HCl and 0.1N NaOH. The pH of the solution was measured with a pH meter (827 pH Lab, Metrohm Ltd., Herisau, Switzerland).

The CS was solubilized in a 1% dilute acetic acid solution (Merck) with a 75–85% degree of deacetylation and mixed with a magnetic stirrer at 100 rpm for 30 min to obtain a 1% stock solution. Stock model wastewater solutions of 1000 mg/L Ni or Zn were prepared by dissolving the required amounts of NiCl₂ or ZnCl₂ in deionized water.

Jar test

Chemical coagulation experiments were carried out using a jar testing technique. Jar testing equipment (JLT6 model, VELP Scientifica, Italy) was used for investigating the effects of pH (6–11), coagulant dosage (5–1000 mg/L), and initial metal ion concentration (3–100 mg/L) on removal of Ni and Zn. A volume of 25 mg/L of prepared PACl or CS solution was added to a jar containing 1000 ml of sample. The coagulation experiments proceeded with rapid mixing of wastewater samples at 120 rpm for 1 min, followed by slow mixing at 30 rpm for 20 min. Sedimentation was allowed to occur for 60 min, and residual metal concentrations were measured after filtration of wastewater using flame atomic absorption spectroscopy (AAS 5FL model, Thuringia, Germany).

RESULTS

The influence of different pH on Zn and Ni removal efficiency was investigated at a concentration metal of 25 mg/L and the coagulant dosage of 25 mg/L [Figure 1]. From Figure 1, initial pH had an important effect on the coagulation behavior of the two coagulants. To determine optimum dosage of CS and PACl, experiments were conducted by changing the dosage of coagulants. The results of this part are shown in Figure 2. As

shown in Figure 2, optimum doses of CS and PACl for both metals were 100 and 500 mg/L, respectively. Moreover, in this study, the dose of the CS (as coagulant aid) was varied from 2 to 25 mg/L. Figure 3 presents that combination of PACl and CS at different ratios achieved better removal efficiencies of the metals in the range of 95.32–99.9% for total Zn and 83.2–99.37% for Ni.

The effect of initial metal concentration on the removal rate was examined with several solutions containing concentrations from 3 to 100 mg/L of single metals. Figure 4 shows the change of the residual concentrations of metals with the initial concentration. As expected, it appears that the removal rate was decreased upon increasing initial concentration. Investigation of metal ions interaction shows that in presence of Zn, removal efficacy of Ni apparently increases [Figure 5].

DISCUSSION

pH effect

pH is one of the effective parameters on solution characteristics, behavior of biopolymer in solution, metals surface charge, and coagulants during coagulation and flocculation process. In this research, the effect of pH on

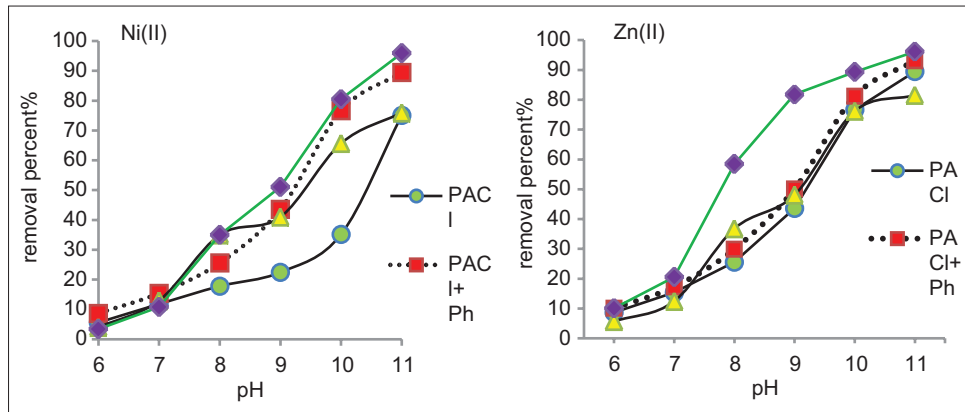


Figure 1: Effect of pH on Zn and Ni removal by chemical coagulation (Zn: 25 mg/L, Ni: 25 mg/L, coagulant dose: 25 mg/L, settle time: 1 h). Zn: Zinc; Ni: Nickel

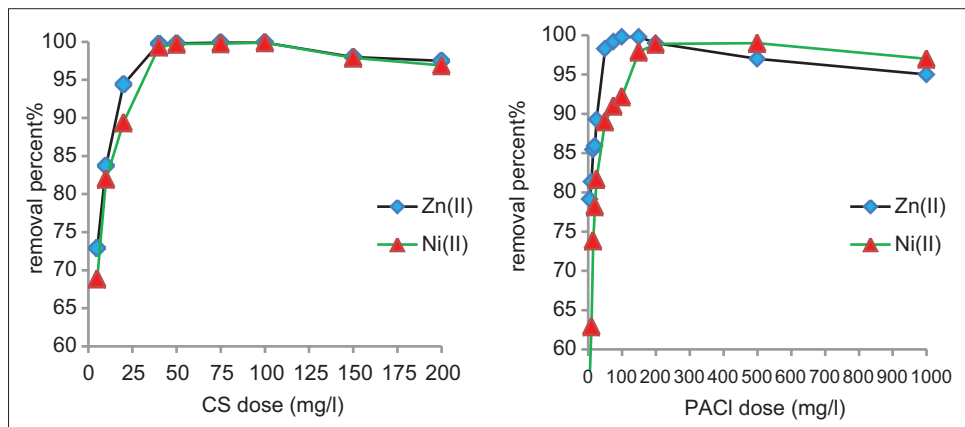


Figure 2: Effect of coagulant dose on metal removal (Zn: 25 mg/L, Ni: 25 mg/L, settle time: 1 h, pH: 11). Zn: Zinc; Ni: Nickel

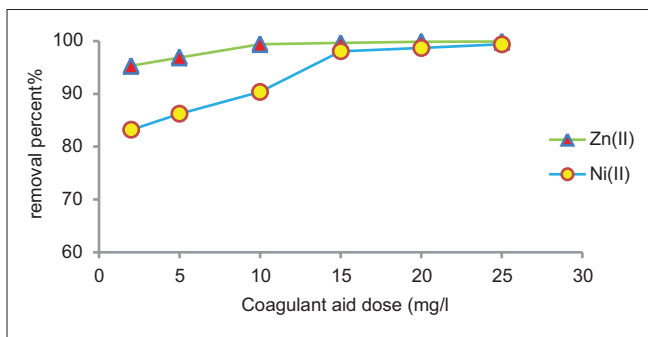


Figure 3: Effect of coagulant aid dose on metal removal (Zn: 25 mg/L, Ni: 25 mg/L, coagulant dose: 25 mg/L, settle time: 1 h, pH: 11). Zn: Zinc; Ni: Nickel

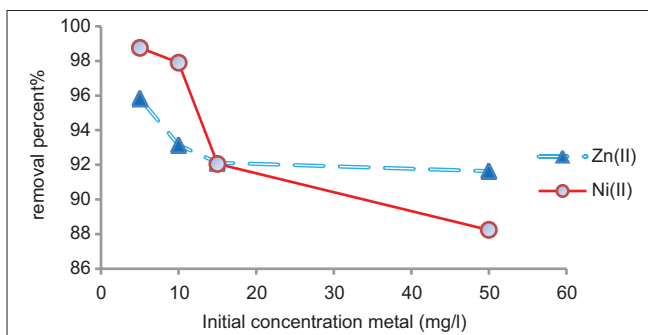


Figure 4: Effect of initial concentration on metal removal (coagulant dose: 25 mg/L, settle time: 1 h, pH: 11). Zn: Zinc; Ni: Nickel

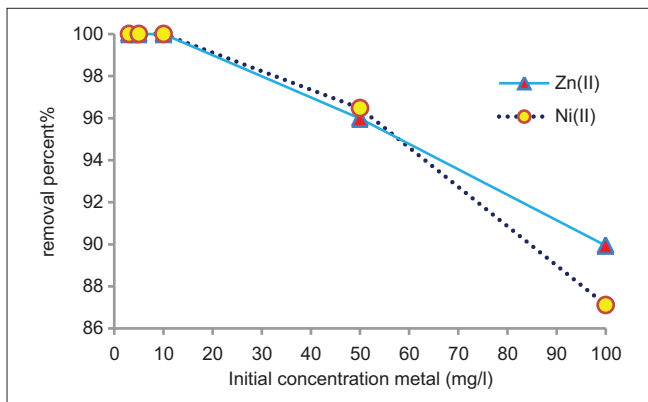


Figure 5: Effect of metal ions interaction on the removal efficiency of metals (pH: 11, coagulant dose: 25 mg/L, aid coagulant: 10 mg/L, settling time: 1 h). Zn: Zinc; Ni: Nickel

coagulation and flocculation process of Zn and Ni using CS and PACI is shown in Figure 1. According to Figure 1, metal removal efficiency by PACI and CS is increased when pH increases. The metal removal percentage of 85% and 96% was obtained by PACI and CS, respectively. This increase of metal removal ratio by PACI can be explained on the basis of groups which were formed through PACI hydrolyzes and effect of pH. At pH values lower or equal to 8, PACI is hydrolyzed into $Al(OH)^{2+}$, $Al(OH)_2^{2+}$, $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, $Al(OH)_3$, and $Al_{13}O_4(OH)_{24}^{7+}$ $Al_3O_4(OH)_{24}(H_2O)_{12}^7$ groups and the removal ratio for Zn and Ni is very low due to cationic

charge of hydrolyzed groups. When pH value increases from 8 to 11, the removal ratio of Zn and Ni is increased through absorption mechanism, which is formed in this pH range by $Al(OH)_3$. For CS, increasing Zn and Ni removal efficiency by increasing pH value can be explained according to CS isoelectric point ($pH_{ZC} = 6.3$). When sample pH is lower than isoelectric point, CS gets positive electric charge because amino groups ($-NH_3^+$) are protonized so that it can react easily with negative charge compounds such as proteins, anionic polysaccharides, fatty acids, and negative charge metals. At pH values over isoelectric point, CS gets negative electric charge because carboxyl group (COO^-) is ionized. Therefore, increase in cationic metal removal percentage (due to pH increase) is related to reduction in cationic sites of amino groups and negative charge increase through ionized carboxyl groups. Researchers in their studies about metal removal through chemical coagulation concluded that as pH rises, the metal removal ratio is increased.^[16,39-41] Also, Bratskaya *et al.* in their research found that removal ratio for Ni and Zn using CS derivatives is improved as pH value is increased.^[42] Furthermore, obtained results in Figure 1 show that Zn and Ni removal ratio using PACI (without pH control) is lower when compared to condition that in which pH is controlled. This reduction in metal removal ratio is related to decrease in aquatic solution's alkalinity after adding PACI (as coagulant). Chu reported that pH value of solution and efficiency of removal ratio are decreased as coagulant increased.^[43]

Determining coagulant dosage

In this study, the effect of coagulant dosage on Zn and Ni removal ratio was evaluated by changing CS and PACI dosage in constant conditions (pH = 11 and initial concentration for Ni and Zn were equal to 25 mg/L). The effect of coagulant dosage on efficiency of Zn and Ni removal ratio in aquatic solutions is shown in Figure 2. From Figure 2, first, by increasing PACI dosage, Zn and Ni removal ratio is increased and then decreased so that the most removal percentage was obtained about 99% at coagulant dosage equal to 150 and 500 mg/L. This initial increase for Zn and Ni removal ratio can be explained due to adding PACI and increase for $Al(OH)_3$. However, reduction for Zn and Ni removal percentage at high dosages (500–1000 mg/L) can be described that by increasing coagulant dosage, coagulated metals become stable again, and return to solution. In addition, obtained results in Figure 2 show that by increasing CS dosage, Zn and Ni removal percentage is increased accordingly, which it is due to diprotonization of amino groups and increasing negative charge because carboxylic group is ionized at optimum pH value. At optimum pH = 11, amino groups' sites (which in diprotonized form) cause to metals attachment through chelate mechanism and carboxylic groups' sites (through ionization) results in charge neutralization and interparticle bridging. In addition, these results can be defined on the basis of charge density. CS has high density comparing other coagulants and metal removal ratio using polymer is

increased as charge density of polymer is raised. Pang *et al.* reported that by increasing PACl dosage, metal removal ratio is increased.^[41] Zazouli and Yousefi in their study reported that by increasing ferric chloride, metal removal ratio raises at first but then reduces. They attributed this reduction for removal ratio (in high concentration of ferric chloride) to formation of fine floc and its effect on settling speed and restabilization of metals.^[44] Chu concluded in his research that at first, the Pb removal ratio by alum is increased, and then reduces due to pH value reduction.^[43] Bratskaya *et al.* reported in their research that metal removal ratio is increased as CS dosage increases.^[42]

Determining effect of chitosan aid coagulant

The effect of CS on Zn and Ni removal ratio was evaluated at constant conditions. Obtained results in Figure 3 show that Ni and Zn removal ratio is increased as CS dosage (as coagulant) increases. This increase may be related to high surface charge and increase anionic charge CS at alkaline pH values. Amuda *et al.* obtained same results and showed the amount of metals removal increased with increasing natural polymers as coagulant.^[45]

Determining effect of initial metal concentration and competitive removal

The effect of initial metal concentration on removal ratio was investigated in initial Zn and Ni concentration (3, 5, 10, 50, and 100 mg/L) at stable condition (Zn: 25 mg/L, Ni: 25 mg/L, coagulant dose: 25 mg/L, CS: 10 mg/L, settle time: 1 h, pH: 11). According to the results from Figure 4, as initial metal concentration increases, Zn and Ni removal ratio from synthetic solution is reduced. This reduction may be related to lack of enough adsorption sites and hydrolyze groups. In other word, the higher initial metal concentration, the more coagulant is needed. In study that conducted by Bojic *et al.*^[3] and Xu *et al.*,^[19] it was recognized that by increasing initial metal concentration, metal removal ratio is reduced. They explained this reduction due to decrease of adsorption site, which is related to saturation of adsorption sites by $\text{Al}(\text{OH})_3$.

In the present research, experiments were conducted in optimum conditions to evaluate the metal interaction on competition removal efficiency of Zn and Ni by PACl and CS. In this stage, metal concentrations equal to 5, 10, 15, and 50 mg/L were used. Obtained results showed that by increasing Zn concentration from 5 to 10 mg/L, Ni removal ratio is increased, meanwhile, when Zn concentration was between 15 and 50 mg/L, Ni removal ratio was decreased. This increase may be related to activation of Zn metal surface (as an adsorbent) which helps Ni removal improvement and also reduction of Ni (when Zn concentration increases from 15 to 50 mg/L) may be related to competition of both metals for produced OH^- (because of pH increase) and also competition about absorption of sites which absorb $\text{Al}(\text{OH})_3$. However, regarding Zn, by increasing Ni concentration,

the Zn removal ratio is decreased dramatically. This reduction may be related to competition between two metals for produced OH^- (because of pH increase) and also competition about absorbent sites. Our results are in agreement with other researchers such as Bojic *et al.* and Pang *et al.*^[3,41]

Comparison between efficiency of polyaluminum chloride and chitosan for zinc and nickel removal

Regarding description of determinant factors (pH, coagulant dosage, and settling time) on Zn and Ni removal from aqueous solutions using PACl and CS, our obtained results showed that CS is more effective than PACl for metal removal at laboratory scale. As shown in Figure 1, CS at pH values equal or less than 9 has the same efficiency for metal removal which PACl has at high pH values. For example, at pH = 9, the Zn removal ratio using CS is equal to 81.8% whereas it is 38.98% if PACl was used at same pH value. Furthermore, this metal removal ratio at pH = 9 by CS is nearly equal to metal removal ratio by PACl at pH = 11. Furthermore, CS has the same high removal efficiency for Zn and Ni (in comparison with PACl) at low dosage (20–40 mg/L) which PACl should be used at higher dosage (100–500 mg/L). Also, this high efficiency at low dosage may be related to high ability of active groups such as amino and carboxyl groups and also little change of pH after addition of CS, meanwhile PACl causes to reduction of solution pH.

CONCLUSION

In the present study, coagulation and flocculation by PACl and CS to remove Zn and Ni metals from aquatic solutions were evaluated. Obtained results showed that optimum pH in coagulation and flocculation processes for both coagulants were 11. At the beginning, increasing in the amount of coagulants led to increasing in Zn and Ni removal efficiencies but then their efficiencies decreased. The most amounts of Zn and Ni removal with CS and PACl were seen in 100 and 150–500 mg/L, respectively. 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. According to the initial metal concentrations which used in this study, the most amounts of Zn and Ni removal efficiencies in coagulation and flocculation were related to 3, 5, and 10 mg/L of metal and in these concentrations, removal efficiencies were 100%. By increasing in the concentration of CS as a coagulant aid, the amount of Zn and Ni removal efficiencies increased. Moreover, according to the obtained results, concurrent presence of Zn and Ni in aqueous solutions leads to reduction of Zn removal (comparing the situation in which each metal is present solely), because presence of metals in aqueous solutions cause to competition on getting produced OH^- and adsorption of metals on $\text{Al}(\text{OH})_3$.

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Conflicts of interest

There are no conflicts of interest.

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