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Novel Material for Nickel Recuperation

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Graft polymerization of N-vinyl-2-pyrrolidone with chitin was studied using hydrogen peroxide for initiation. The capacity of the obtained VP-g-Ch graft copolymer for adsorption of nickel was examined. The effect of temperature, pH and solute concentration on the chelating properties of the grafted and ungrafted chitin were determined. The thermal profiles obtained showed higher thermal resistance for the VP-g-Ch than chitin. The results indicate that the obtained graft copolymer under investigation is a potentially powerful ion exchanger that can be employed for heavy metals removal from wastewater effluents.

Keywords: *chitin, grafted chitin, vinylpyrrolidone, nickel removal*

1. Introduction

Heavy metal ions resultants of the chemical process industries are pollutants that have received a careful attention of the governmental organizations since they can be absorbed by plants and animals and then concentrated in the foods.

Many different natural and synthetic materials with chelating properties have been developed for use in chemical processes industries plants for preventing operational problems or contamination of the environment.

Chitin, poly[b-(1 → 4)-2-acetamido-2-deoxy-D-glucopyranose], a polysaccharide closely related structurally to cellulose is the major structural component of the exoskeleton of invertebrates and the cell walls of fungi[1].

Since the biodegradation of chitin is very slow in crustacean shell waste, accumulation of large quantities of discards from processing of crustaceans has become a major concern in the seafood processing industry.

The nontoxic, biodegradable and biocompatible properties have been of interest in the past few decades to a wide range of industrial applications including bioconversion for the production of value-added food products[2], preservation of foods from microbial deterioration[3], clarification and deacidification of fruit juices[4], formation of biodegradable films and coatings for aliments[5], recovery of waste material from food processing discards and purification of water[6-7].

Nickel is a metal commonly used in a series of industrial processes such as electroplating, plastics, pigments, electrical contacts, alloys, ceramics and nickel-cadmium batteries.

In this work the complexing ability of N-vinyl-2-pirrolidone-*graft*-chitin (VP-*g*-Ch) graft copolymer was investigated with respect to the adsorption of Ni^{+2} from aqueous solution.

2. Experimental

Chitin was isolated from exoskeleton of pink shrimp (*Solenocera* melantho) shell waste, after treated with 2.5 N NaOH (10 mL per gram of shrimp shell at room temperature for 8 h) and 1.7 N HCl (10 mL per gram of shrimp shell at room temperature for 8 h)[8]. After being washed with distilled water until pH was neutral and dried at 90 °C for 48 h, the obtained chitin was milled and screened to separate a 100 mesh fraction.

The preparation of the VP-*g*-Ch graft copolymer was prepared by the condensation reaction between chitin and vinyl-2-pirrolydone promoted by H_2O_2 (70 cm^3 H_2O_2 23%/kg chitin). Chitin was mixed with the N-vinyl-2-pyrrolidone (NVP) solution in a glass –stoppered flask and mixed thoroughly. After copolymerization, the reaction products were extracted with ethanol-water mixture (1:1 v/v) to remove ungrafted poly(N-vinyl-pyrrolidone).

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The thermal properties of chitin and VP-*g*-Ch was studied by thermogravimetry (TGA) in a Mettler TGA 40, from 20 to 800 °C, 5 °C/min, using opened aluminum pans and under nitrogen.

In adsorption experiments, a fixed amount of dry chitin and VP-*g*-Ch (1.0 g) and 10 dm^3 of an aqueous phase were placed in a 0.25 dm^3 glass-stoppered flask and shaken at 130 rpm using a thermo stated shaker bath (Firstek model B 603).

After filtration, the concentration of Ni^{+2} was analyzed using an atomic spectrophotometer (GBHC model 932). Each experiment was triplicated under identical conditions.

3. Results and Discussion

Figure 1 shows the mechanism for the graft reaction of the N-vinyl-2-pyrrolidone (VP) onto chitin (Ch). The hydrogen peroxide H_2O_2 has been reported to be an effective system for initiating the grafting of vinyl monomers onto

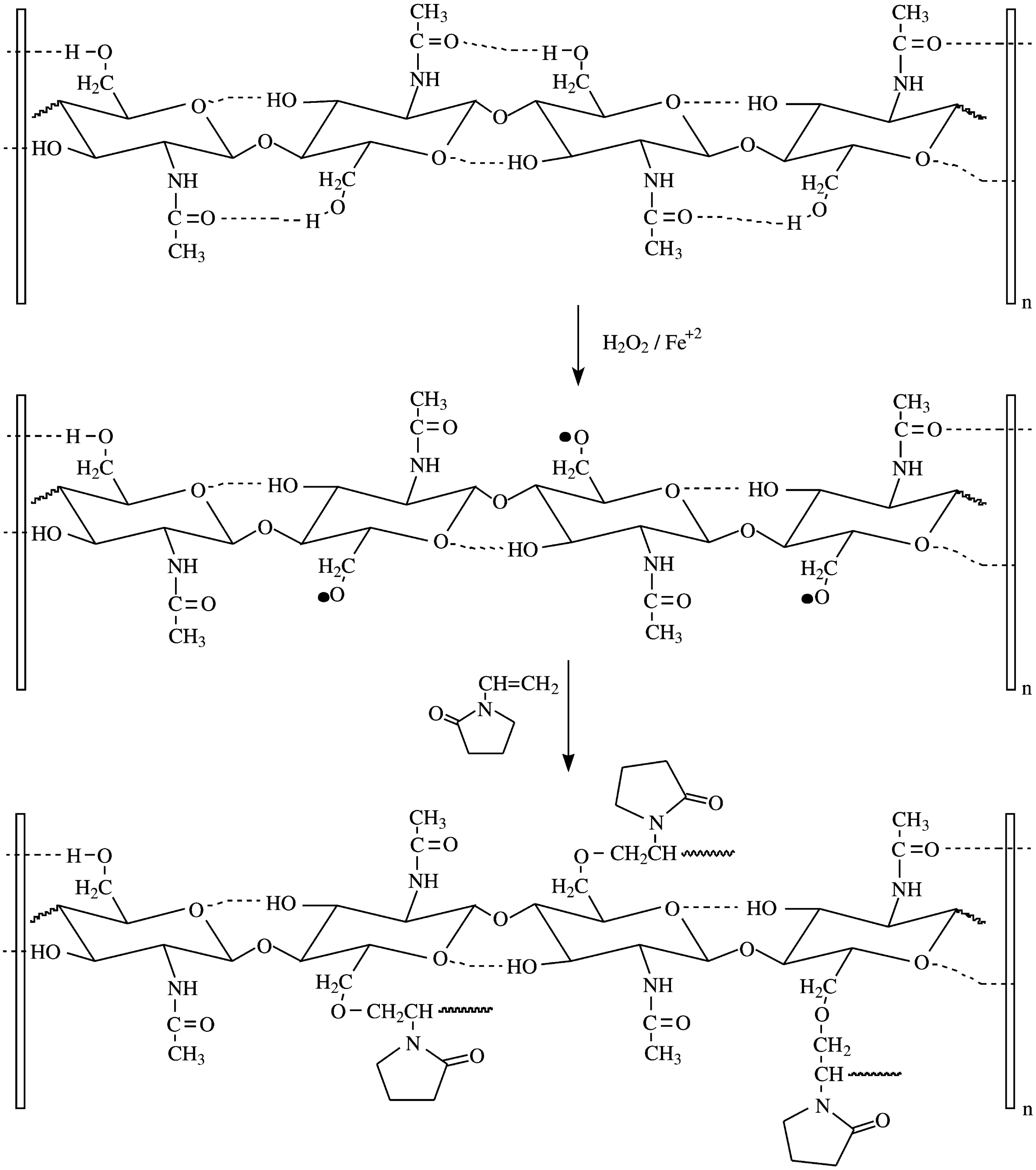

Figure 1. Proposed mechanism of the graft reaction of N-vinyl-2-pyrrolidone onto chitin catalyzed by the H_2O_2/Fe^{+2} system.

carbohydrates[8]. Abstraction of hydrogen atoms from chitin hydroxyl groups by the created radicals leads to the formation of chitin macro radicals. In the presence of vinyl-2-pyrrolidone, grafting occurs by the addition of the chitin macro radical to the double bond of monomer. This is followed by the addition of further monomer molecules to give rise ultimately to graft copolymer (Fig. 1).

Figure 2 shows the effect of VP concentration on the graft yield. Increasing the VP concentration to 80% was accompanied by a significant decrease in yield. This suggests that chitin underwent chemical changes under the influence of the grafting system. Such changes seem to have converted the chitin to a substrate with no further susceptibility towards grafting. It is likely that the grafted poly(N-vinyl-2-pyrrolidone) acts as a diffusion barrier, thereby preventing the further polymerization of VP with chitin, even if the former is used at as high concentrations as 80%.

Figure 3 illustrates the adsorption of Ni^{+2} in the chitin and VP-*g*-Ch as a function of time. In this case, the solution pH was adjusted to 4.6. A maximum adsorption capacity of around 0,09 mol/L at 90 min is obtained, comparable to that obtained for 0,0090 mol/L adsorption for unmodified chitin. It shows that the adsorption of Ni^{+2} remained constant, implying that equilibrium has been reached.

Adsorption isotherms for Ni^{+2} as a function of solute concentration are shown in Fig. 4. More Ni^{+2} was adsorbed on VP-*g*-Ch than in chitin. The present result indicates that the vinyl-2-pyrrolidone graft copolymerization is a very suitable technique to increment the metal sorption properties of chitin.

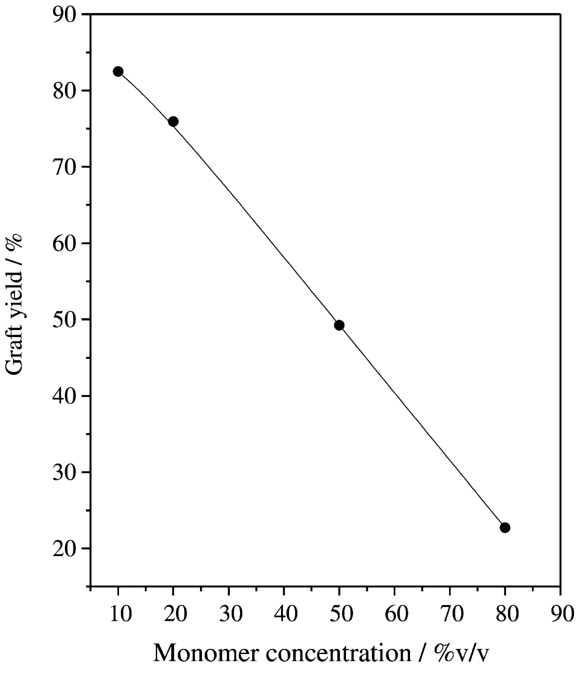

Figure 2. Influence of monomer concentration on copolymerization of N-vinyl-2-pyrrolidone with chitin.

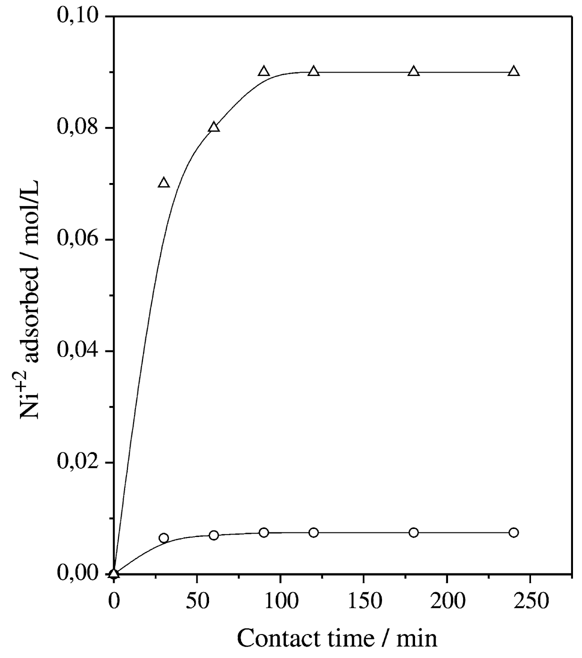

Figure 3. Adsorption isotherm of Ni^{+2} on chitin (O) and VP-g-Ch (Δ) at 298 K.

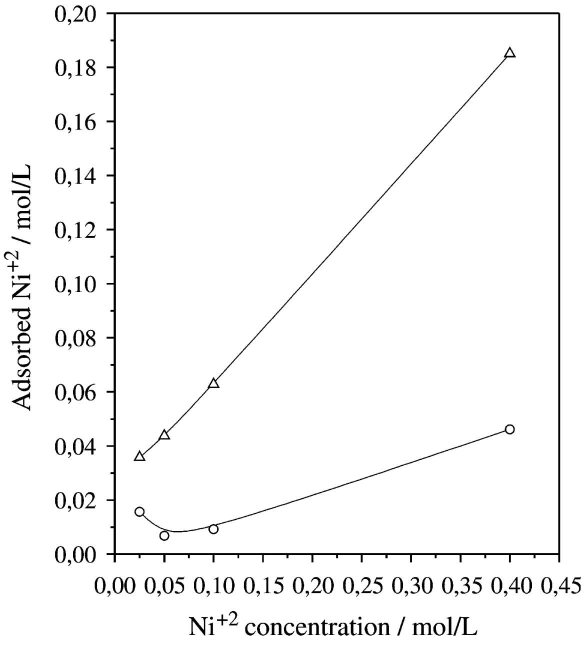

Figure 4. Adsorption isotherm of Ni^{+2} on chitin (O) and VP-g-Ch (Δ).

The influence of temperature on the adsorption rate was studied. One of the more widely used methods of describing this effect is the Arrhenius relationship[9]:

$$k = Ae^{(\frac{-E_a}{RT})}$$

where E_a is the apparent activation energy which represents minimum energy for reaction to occur, and A is the frequency factor, which is independent of temperature. The Arrhenius equation may be written in logarithmic form as:

$$\ln k = \ln A - \frac{E_a}{RT}$$

so that a linear relation occurs between ln k and 1/T. In Fig. 5, the k values have been plotted as a function of inverse of absolute temperature. The apparent activation energy, E_a, was calculated for the Ni^{+2} adsorption on chitin and on VP-*g*-Ch. The E_a value was calculated for the adsorption of Ni^{+2} on chitin and VP-*g*-Ch which yields E_a of 69 and 13 cal/mol, respectively.

The value of the activation energy of VP-g-Ch is five order of magnitude smaller than chitin, which indicated that the chelation of metal on the VP-*g*-Ch takes place relatively easily.

Figure 6 shows the effect of pH on the percentage adsorption of Ni^{+2} on chitin and VP-*g*-Ch. The percentage adsorption increases with increasing pH. It was known that chitin shows chelating ability toward a number of metal ions due to its amide groups that could act as electron donors[10]. Thus, the nitrogen electrons present in the amide groups can establish dative bonds with Ni^{+2} ions. The superior chelating ability of VP-g-Ch was due to pyrrolidone rings in the grafted VP and due to a significant freedom of the grafted VP chains that may impart low conformational rigidity compared to chitin[11].

Figure 7 present the thermal analysis of chitin and VP-*g*-Ch, respectively. The results obtained indicate that the graft copolymer VP-*g*-Ch (G: 20% m/m) is lightly more stable at higher temperatures than chitin. Enhancement of the chitin thermal stability with the grafting degree could be associated with some reticulation of the grafted chains due to the increasing abundance of primary free radical species. This increase in thermal stability may be useful in

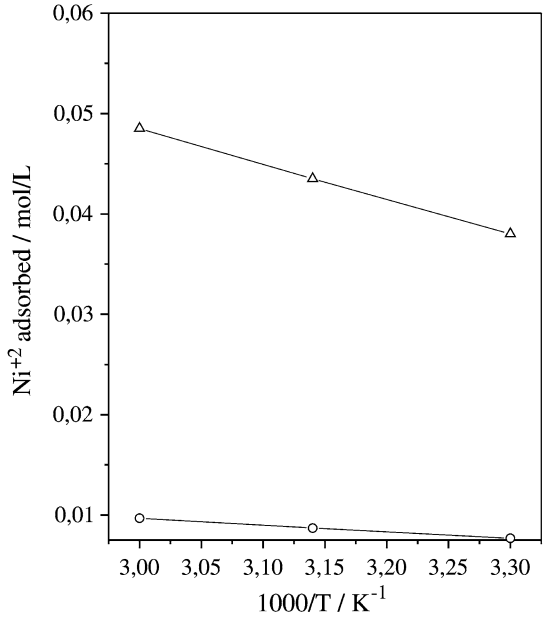

Figure 5. Arrhenius plot to determine activation energy for adsorption of Ni^{+2} on chitin (O) and VP-g-Ch (Δ).

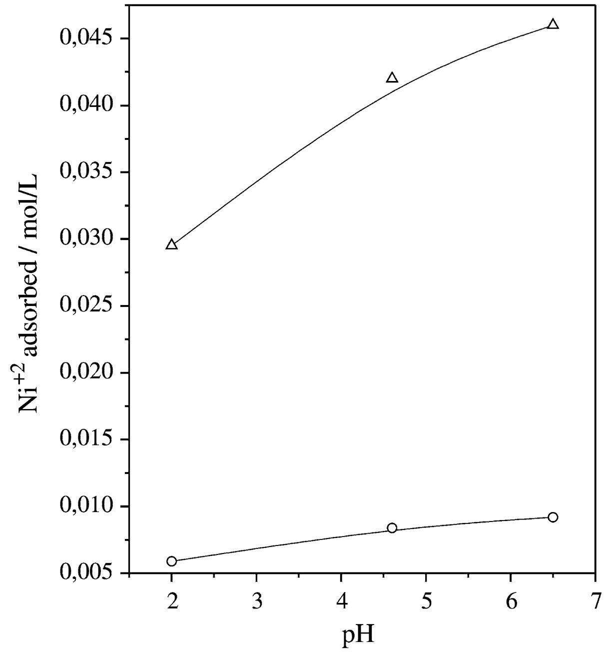

Figure 6. Effect of pH for the Ni^{+2} adsorption on chitin (O) and VP-g-Ch (Δ).

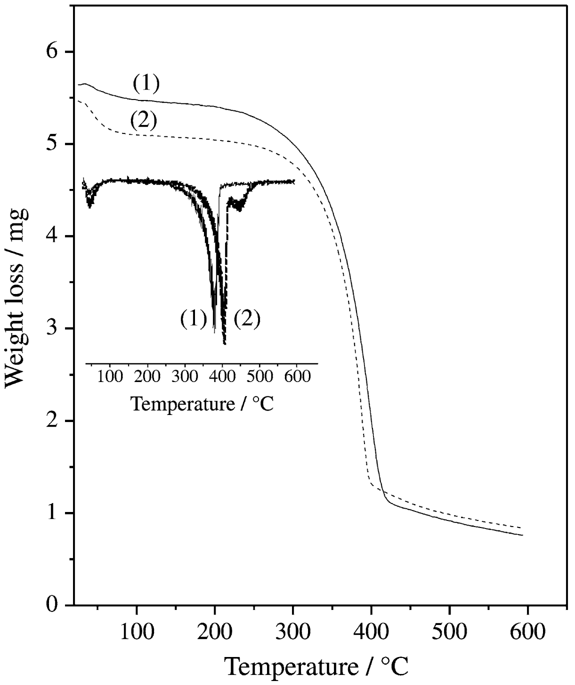

Figure 7. Thermogravimetric analysis of chitin and grafted chitin in N_2 atmosphere. Chitin (1), VP-g-Ch (2), (G: 20% m/m).

engineering processes where the remove process of the heavy metal may be at higher temperatures.

4. Conclusions

The capacities of Ni^{+2} adsorption using vinyl-2-pyrrolidone grafted chitin from aqueous solution have been measured. The graft coplymer VP-*g*-Ch shows an excellent ability for Ni^{+2} adsorption. The improvement in the Ni^{+2} adsorption capacity by VP grafting of chitin could be interpreted in terms of increased swellability as well as the presence of nitrogen electrons in VP unities that can establish dative bonds with Ni^{+2} ions. Thus, the presence of poly(vinyl-2-pyrrolidone) graft in the molecular structure of chitin disrupts its structure and, in turn, better diffusion from the aqueous phase to the adsorbent phase is achieved. This work provides useful data for adsorption removal of Ni^{+2} from aqueous solutions.

5. References

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