PREPARATION AND EVALUATION OF GRAFT COPOLYMER BASED ON SHRIMP CHITIN AND ACRYLONITRILE FOR WASTE WATER TREATMENT

2. Adsorption Capacity of Amidoximated Chitin-g-poly(acrylonitrile) Copolymer for Copper(II) Ion from Aqueous Solution

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Amidoximated chitin-g-poly(acrylonitrile) copolymer was prepared by a reaction between hydroxylamine and cyano group in chitin-g-poly(acrylonitrile) copolymer prepared by grafting acrylonitrile onto shrimp chitin using chitin thiocarbonate-Fe(II)-hydrogen peroxide redox system as an initiator. The adsorption and desorption capacities of amidoximated chitin-g-poly(acrylonitrile) copolymer for the copper(II) ion in aqueous solution were carried out in aqueous solution. The effects of graft yield, pH of the solution, treatment time, temperature, and metal ion concentration on adsorption capacity were studied. The experimental results showed that this graft copolymer was far more effective than original chitin for removing copper(II) ion in all experiments. Desorption and readsorption of copper(II) ions onto this copolymer were also investigated.

INTRODUCTION

Chitin is the most abundant natural amino polysaccharide and estimated to be produced annually almost as much as cellulose. It has become of great interest not only as an underutilized resource but also as a new functional material of high potential in various fields, and the recent progress in chitin chemistry is quite noteworthy. Special attention has been given to the chemical modifications of chitin as one of the most probable means to realize its full potential. Reactions with chitin have been carried out mostly on solid chitin owing to the lack of solubility in ordinary solvents [1]. Graft copolymerisation on polymer has been employed as an important technique for changing its physical and chemical properties. Graft copolymerisation reactions of vinyl monomers on chitin, using redox initiator and by a photoinduced method, have recently been explored as an interesting alternative chemical modification required to develop new natural/synthetic polymer hybrid materials. These graft copolymers are of importance in view of new industrial application such as water absorbents, ion exchangers, flocculants, membranes, modified electrodes and, principally, chelating agents[2]. Among these polymers containing the amidoxime group derived from poly(acrylonitrile) (PAN) or its copolymer have received much attention and were found to have high adsorption properties for heavy metal ions, such as cadmium ion [3]. In previous article [4], we reported the preparation chitin-g-poly(acrylonitrile) copolymer (ChAN) by grafting acrylonitrile onto shrimp chitin using chitin thiocarbonate-Fe(II)-hydrogen peroxide redox system as an initiator.

Although many metal elements are essential for human to keep health, but too high concentration will be harmful to health. For example, too high concentration of Cu^{2+} in blood will lead copper poisoning and recent research even show that it has something to with the occurrence and development of some cancers. Furthermore, the wide application of copper metal in industry, especially in electroplate accounts for its importance, but it also caused much industrial waste water containing Cu^{2+} which pollutes the environment. How to remove the metal ions from liquid waste is studied extensively, chitin and its derivatives were found to be efficient chelating agents for Cu^{2+}[5], so the aim of this present work is to investigate the usability of amidoximated chitin-g-poly(acrylonitrile) copolymer for the removal of copper(II) ions from an aqueous solution.

EXPERIMENTAL

Materials and methods

α-Chitin was extracted from shrimp shell, by modified Hackman method [6], dried *in vacuo* at 60°C, purified by extracting with methanol [7] and powdered to a 50 mesh size before use. The degree of deacetylation (DA) found by elemental analysis [8] was about 0.15. Acrylonitrile (AN) (reagent grade, China) was purified by distillation under reduced pressure before use. All other commercial available chemicals were analytical grade.

Infrared (IR) spectra were recorded on IMPACT-410 Fourier-transform IR (FTIR) spectrometer (Germany) with the potassium bromide technique.

Preparation of adsorbent (amidoximated)

ChAN was obtained by grafting acrylonitrile onto shrimp chitin using chitin thiocarbonate-Fe(II)-hydrogen peroxide redox system as an initiator **ChAN** [4]. Graft yield (GY) is defined as follows: $GY\ (\%) = \frac{w_1 - w_o}{w_o} \times 100$

where w_0 and w_1 are weights of original and grafted samples, respectively.

The general synthetic procedure for the preparation of amidoximated ChAN (a-ChAN) [4,10] is summarized here. One gram of ChAN (controlled PAN graft yield) and 100mL of 5% hydroxylamine solution (prepared by mixing of 5.55 wt% $NH_2OH.HCl$ solution and 3.60wt% NaOH aqueous solution) were stirred by magnetic stirrer at 75°C for 6h. Finally, a-ChAN was obtained by washing several times with distilled water and drying at vacuum at 60°C to constant weight.

Adsorption and regeneration studies

The adsorbate solution was prepared by dissolving $CuSO_4.5H_2O$ in distilled water. Adsorption experiments were conducted by stirring an accurately weighed amount of the adsorbent (100mg chitin or a-ChAN) with 50mL of the Cu(II) ion solution of predetermined concentrations and pHs in 100mL stoppered bottles by magnetic stirrer for a desired durations at various specified temperatures. pH of the solution was controlled by mixture acetic acid - sodium acetate buffer solution. The pH was varied from 3 to 7. At predecided intervals of time, the mixture was filtered and the Cu(II) ion concentration of the filter liquor was measured by atomic absorption spectroscopy (ANS, PERKIN-ELMER-3300, USA). The adsorption capacities of chitin and a-ChAN were evaluated using the following expression:

$$Q = \frac{V \times (C_0 - C)}{W}$$

where Q is the adsorption capacity (mmol metal ion/g adsorbent), V is the volume of metal ion solution (L), C_0 is the concentration of metal ion before adsorption (mmol/L), C is the concentration of metal ion after adsorption (mmol/L), and W is the weight of absorbent (g).

50mL of 0.1N hydrochloric acid was added to a glass-stoppered bottle containing 0.1g polymer (chitin or a-ChAN) with adsorbed Cu(II) ions. The mixture was stirred by magnetic stirrer for 10 hours at room temperature and filtered. The adsorbed a-ChAN after desorbing was dried under vacuum at 60°C to constant weight, then used for readsorbing Cu(II) ion. Finally, the adsorption capacity after every adsorption-desorption cycle was obtained by the same above method.

RESULTS AND DISCUSSION

Preparation of adsorbent

The optimum conditions for graft copolymerization of AN onto chitin were investigated by observing the effect of ferrous ammonium sulfate (FAS), hydrogen peroxide and monomer concentrations as well as pH of polymerization solution, reaction time and reaction temperature on the graft yield in detail [4]. As Aly Sayed Aly et al. reported that, chitin-g-PAN copolymer was converted into amidoximated chitin-g-PAN copolymer by the reaction between hydroxylamine and cyano group in ChAN. The FT-IR spectra of chitin, ChAN and a-ChAN are shown in Figure 1. As shown in previous results [4], a new peak, characterized as the —C≡N stretching vibration at 2247cm^{-1}, was found in ChAN in Figure 1(b). After amidoximation of ChAN, the -C≡N peak vanished and a strong, broad adsorption band centered at 1666 cm^{-1} appeared. This peak could be a mixture of the amide I band of main chains and the -C=N- stretching vibration band of amidoximated PAN branches.

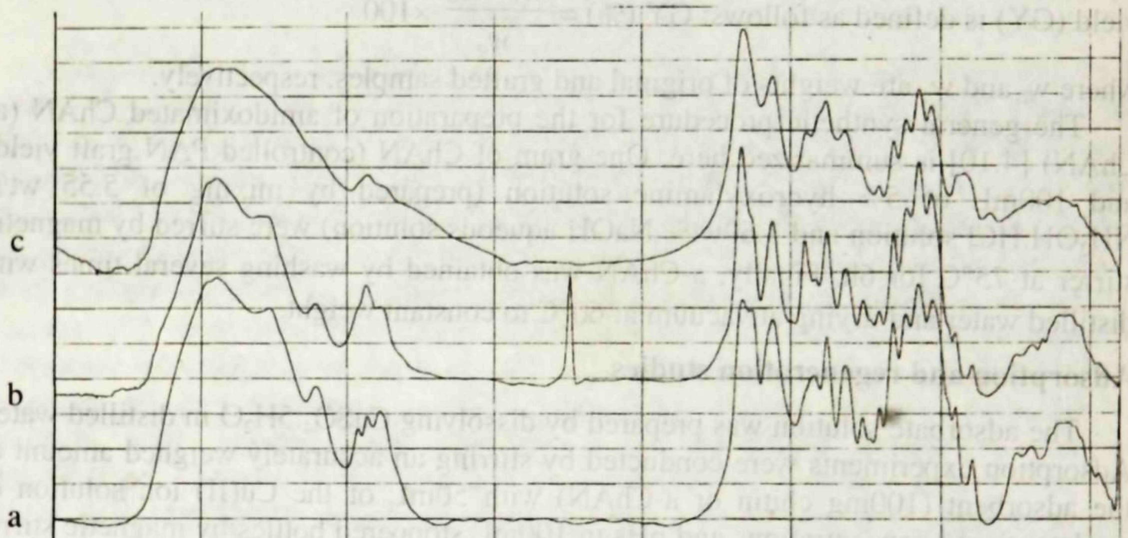

Figure 1: **FT-IR spectra of chitin (a), ChAN (b) and a-ChAN (c).**

Adsorption and regeneration studies

Adsorption mechanism on chitin was shown [9]. The effects of graft yield, pH of the solution, treatment time, and metal ion concentration on adsorption capacity for Cu(II) ion are shown in Figures 2, 3 and 4.

Figure 2 shows that Cu(II) ion amounts were adsorbed on chitin and a-ChAN with various graft yields at different pH values (3-7), with all other conditions being constant. It is clear that the data indicate the following.

1. The adsorption capacity of Cu(II) ion increases significantly with increasing the pH values up to 6.5 for both chitin and a-ChAN, and then levels off. This is due to less stability of the formed chelates in highly acidic medium.

2. The results of adsorption behavior of the a-ChAN also indicate that the adsorption ability of Cu(II) ion increases with increasing the graft yield within the range studied. The increase in the adsorption with increasing graft yield may be attributed to a higher surface area and more active sites. The amidoximated cyano groups of PAN-grafted chitin are responsible for the interaction of the metal ions with the adsorbent.

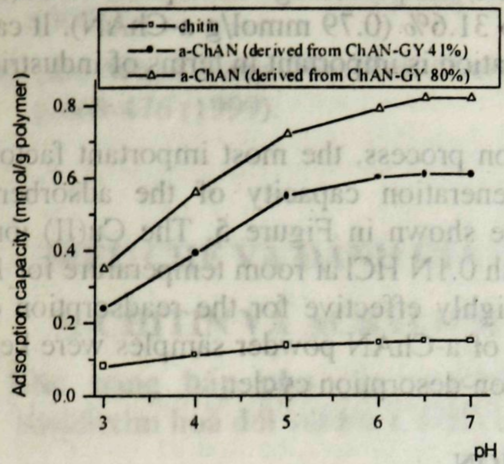

Figure 2. **pH dependence of Cu(II) ion amount adsorbed by chitin and a-ChAN with various graft yields. Time, 5h; temperature, rt; Cu(II) ion concentration, 5mM.**

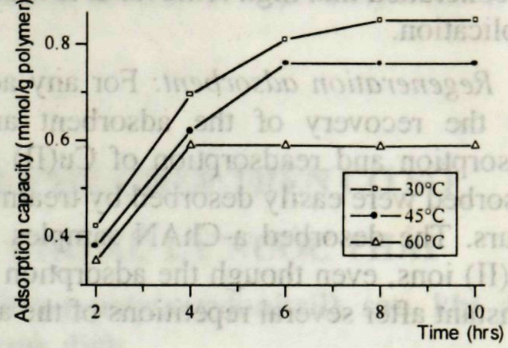

Figure 3. **Effect of time on adsorption capacity of a-ChAN (derived from ChAN-GY 80%) for Cu(II) ions at various temperatures. pH, 6.0; Cu(II) ion concentration, 5mM.**

Figure 3 shows that Cu(II) ion amounts were adsorbed on chitin and a-ChAN with different durations and various initial concentrations, while keeping all other conditions constant. As can be seen in Figure 3, the data show the following.

1. The adsorption capacity of Cu(II) ion decreases on raising treatment temperature. This could be due to the higher stability of formed chelates at lower temperatures, as is generally observed for low-molecular-weight complexes.
2. The adsorption capacity of Cu(II) ion increases with increasing treatment duration to reach maximum value of the equilibrium state and then levels off. The maximum adsorption values occur after 8h, 6h and 4h at 30°C, 45°C and 60°C, respectively.

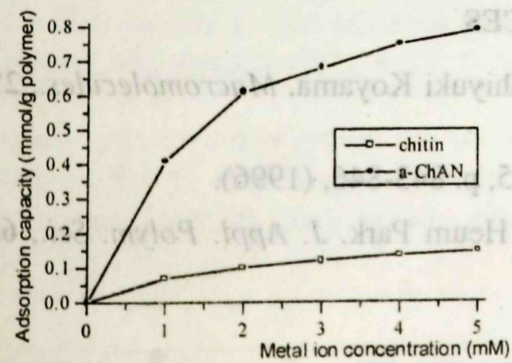

Figure 4. **Effect of metal ion concentration on adsorption capacities of chitin and a-ChAN (derived from ChAN-GY 80%) for Cu(II) ions. Temperature, rt; pH, 6.0; contact time, 5h.**

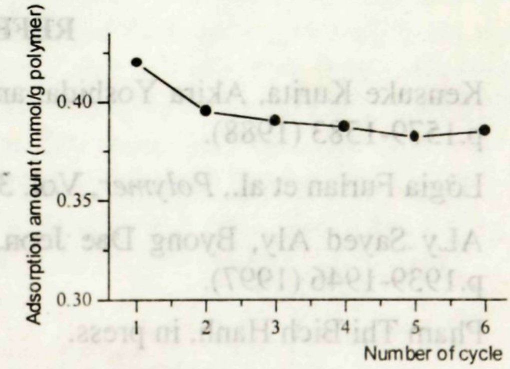

Figure 5. **Adsorption-desorption cycles of Cu(II) ions on a-ChAN (derived from ChAN-GY 80%). temperature, 30°C; pH, 6.0; contact time, 2h; Cu(II) ion concentration, 5mM.**

The adsorption capacities of chitin and a-ChAN for Cu(II) ions from aqueous solution were investigated at various metal ion concentrations (Figure 4). In Figure 4, it is can be seen that the adsorption capacity increases as the concentration of Cu(II) ions increases for both chitin and its graft copolymer (a-ChAN). Obviously, chitin was outstandingly enhanced to remove Cu(II) ions through graft copolymerisation of AN at any metal ion concentration. Nevertheless, with change in the metal ion concentration of the solution from 1mM to 5mM, the percentage adsorption of Cu(II) decreased from 84% (0.42 mmol/g a-ChAN) to 31.6% (0.79 mmol/g a-ChAN). It can be concluded that high removal at low concentration is important in terms of industrial application.

Regeneration adsorbent: For any adsorption process, the most important factors are the recovery of the adsorbent and regeneration capacity of the adsorbent. Desorption and readsorption of Cu(II) ions are shown in Figure 5. The Cu(II) ions adsorbed were easily desorbed by treatment with 0.1N HCl at room temperature for 10 hours. The desorbed a-ChAN samples were highly effective for the readsorption of Cu(II) ions, even though the adsorption ability of a-ChAN powder samples were kept constant after several repetitions of the adsorption-desorption cycle.

CONCLUSION

1. The results show that the adsorption process was affected by the graft yield. The high metal binding ability is achieved by cooperative action of the plural functional groups including the amidoximated cyano groups of PAN branches and acetamido groups of main chains.
2. The adsorption capacity of amidoximated chitin-g-poly(acrylonitrile) copolymer for Cu(II) ion decreases on raising treatment temperature.
3. 8 hours of treatment time was found sufficient to reach the adsorption equilibrium value.
4. The reactive graft copolymer is stable and able to be recycled by acid without losing its activity.
5. The results indicate the adsorption capacity of acrylonitrile grafted chitin is remarkably high, so that the prepared product could be used as a good adsorbent in the cycling of Cu(II) ion through withdrawal from wastewater and seawater.

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ĐIỀU CHẾ VÀ ĐÁNH GIÁ COPOLYME GHÉP TRÊN CƠ SỞ α-CHITIN VÀ ACRYLONITRIL CHO XỬ LÝ NƯỚC THẢI

2. Khả năng hấp phụ của copolyme chitin-g-poly(acrylonitril) sau khi đã amidoxim hoá đối với ion Cu(II) trong dung dịch

Amidoxim hoá copolyme chitin-g-poly(acrylonitrile) được tiến hành bằng phản ứng giữa hydroxylamin với nhóm xyanua của copolyme chitin-g-poly(acrylonitrile) điều chế từ phản ứng ghép acrylonitril lên α-chitin với hệ khơi mào chitin thiocacbonat-Fe(II)-hydro peoxit. Các yếu tố ảnh hưởng đến khả năng hấp phụ như phần trăm ghép, pH của dung dịch, thời gian, nhiệt độ xử lý và nồng độ ion kim loại đã được nghiên cứu. Giải hấp phụ và tái hấp phụ ion Cu(II) lên copolyme này cũng đã được khảo sát.