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Pre-irradiation grafting of acrylonitrile onto chitin for adsorption of arsenic in water

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HIGHLIGHTS

- Partially deacetylated chitin was used for grafting AN by pre-irradiation.
- The maximal grafting degree of AN onto chitin was 114%.
- The cyano- of AN was converted into amidoxime to enhance adsorption.
- The adsorption capacity of As(III) onto modified chitin was 19.724 mg/g.
- Removal of arsenic in groundwater samples was tested by continuous adsorption.

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ABSTRACT

Radiation-induced grafting is an effective technique for preparation of novel materials. In this study, partially deacetylated chitin with deacetylation degree (DDA) of about 40% was graft-copolymerized with acrylonitrile (AN) by a γ-ray pre-irradiation method. The maximal grafting degree of AN onto pre-irradiated chitin at 25 ± 1.2 kGy was 114% for AN concentration in dimethylformamide of 40% (v/v) at 70 °C for 8 h. The mixture ratio of 0.1 N $NH_2OH \cdot HCl$ to 0.1 N NaOH was selected to be 7:3 (v/v) for amidoxime conversion of cyano-groups on grafted chitin (Chi-g-AN). The characteristics of modified chitin were depicted by the FT-IR spectra, BET area and SEM images. Adsorption equilibrium of As(III) onto Chi-g-AN converted amidoxime (Chi-g-AN-C) fits with the Langmuir model and the maximal adsorption capacity was 19.724 mg/g. The break-through times of As(III) on Chi-g-AN-C in column adsorption experiments increased with the increase in bed depths.

1. Introduction

Modification of polymer by radiation grafting techniques has been applied to prepare novel materials, including adsorbents for environmental and industrial applications (Tamada, 2004; Chen et al., 2007). A large amount of free radicals is produced in the irradiated polymer without the use of chemical initiators and these radicals easily reacted with a functional monomer by covalent bonds to form macromolecular chains. In this way, the polymer properties were improved and thus the graft copolymerization was commonly used.

In the past decades, besides studying the degradation effect of natural polymers by radiation, modification by grafting monomers on these substrates has also been carried out by many scientists (Barakat, 2011; Boddu et al., 2008; Laus et al., 2010). Chitin and its deacetylated form chitosan are bio-renewable, biodegradable, biocompatible, inexpensive and environmentally friendly polymers. Chitin is a heteropolymer made up of β-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranose units. It can be extracted from crustacean shell such as prawns, crabs, fungi, insects and other crustaceans (Wan Ngah and Isa, 1998).

Chitosan can be used as an adsorbent to remove heavy metals and dyes due to the presence of amino and hydroxyl groups, which can serve as the active sites (Wu et al., 2001). The heavy metal ions such as As(III), As(V), Cd^{2+}, Hg^{2+} and Pb^{2+} in the groundwater and industrial wastewater caused pollution. High arsenic concentration in groundwater has been reported recently from USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, Japan and India (Mohan and Pittman, 2007). The current WHO recommended guideline value for arsenic in drinking water is less than 10 μg/l, whereas many countries are still having a value of 50 μg/l (Jack et al., 2003). Especially, in

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Vietnam the water from Red River delta with average arsenic concentrations of 159 mg/l threatened human health (Kien and Ross, 2009). Chitosan has been extensively investigated as adsorbents (Wan Ngah et al., 2011). However, chitosan is very sensitive to pH as it can either form gel or dissolve depending on the pH values (Chiou et al., 2004). Therefore chitin is a potential starting polysaccharide to modify for application in different fields, including metal ion adsorbents for wastewater treatment. Chitin even with low adsorption capacity of metal ion exhibits good stability and insolubility in acidic media, is also available in large quantity and a recyclable material that can be used for modification. In order to enhance the adsorptive property of chitin, partially deacetylated chitin has been prepared and used at the same time to modify through grafting with functional monomers. In this work, acrylonitrile monomer was grafted onto deacetylated chitin with DDA of about 40% by a pre-irradiation method; then the cyano-groups (–CN) were converted into amidoxime groups ($-C(NH_2)=N-OH$) by treatment with hydroxylamine (NH_2OH) to enhance the adsorption capacity. The resultant chitin was used for adsorption of arsenic from aqueous solutions of arsenic salt and groundwater samples.

2. Experimental

2.1. Materials

Shrimp shell chitin was supplied by a factory in Vung Tau province, Vietnam. Chitin was further deacetylated in 30% sodium hydroxide at 30 °C for 24 h to obtain a degree of deacetylation (DDA) of about 40%. This value was determined based on FT-IR spectra according to absorbances of chitin at 1320 and 1420 cm^{-1} (Brugnerotto et al., 2001). All other chemicals, including acrylonitrile (AN), hydroxyl ammonium chloride ($NH_2OH.HCl$), tetrahydrofuran (C_4H_8O), N,N-dimethylformamide ($HCON(CH_3)_2$), and sodium arsenite ($NaAsO_2$), were of analytical reagent grade.

2.2. Grafting acrylonitrile onto pre-irradiation chitin and modification of poly-acrylonitrile grafted on chitin

Chitin flakes from shrimp shells with DDA of about 40% were irradiated in air by γ- rays in the dose range from 4 to 35 kGy at a dose rate of 1.3 kGy/h under ambient conditions. The gamma-irradiation dose was determined by using an ethanol–chlorobenzene (ECB) dosimetry system from mean value of absorbed doses of three dosimeters at 30 °C (ASTM International, 2004). Pre-irradiated chitin was immersed into a glass flask containing acrylonitrile (AN) in dimethylformamide (DMF) with ratios from 10:100 to 70:100 (v/v) and Mohr's salt additive of 0.1% (w/v). The flask was connected to a reflux system and heated by an electric oven at 70 °C for 8 h. The AN grafted chitin (Chi-g-AN) was extracted with tetrahydrofuran to remove homopolymers and unreacted monomers and then dried in a forced air oven at 60 °C. The degree of grafting (DG) was calculated from the weight gain as follows:

$$DG(\%) = 100(W_1 - W_0)/W_0 \quad (1)$$

where W_0 and W_1 are the weights of the original and grafted samples, respectively.

The Chi-g-AN was converted to amidoxime by hydroxyl amine (NH_2OH) in sodium hydroxyl (NaOH) at the ratios of 7:3, 1:1 and 1:0 (v:v) at 70 °C to introduce the functional adsorption units. The content of substituted amidoxime groups was determined by titration. The converted Chi-g-AN (Chi-g-AN-C) was immersed in 100 ml of 1 M NaCl aqueous solution and equilibrated for 24 h. For this purpose, the $NH_2–C=N–OH$ group was converted to $NH_2–C=N–ONa^+$. The exchange proton from amidoxime group was titrated with a 0.05 N NaOH solution. The content of amidoxime group (M) was determined as follows:

$$M(\text{mmol/g}) = (0.05V_{NaOH})/W_d \quad (2)$$

where V_{NaOH} is the volume of 0.05 N NaOH solution and W_d is the dried weight of Chi-g-AN-C.

2.3. Characteristics of modified chitin

The modified chitin samples were characterized by FT-IR (Fourier Transform Infrared Spectrophotometer) spectra with an FTIR – 8400s (Shimadzu, Japan). The change of surface morphology of chitin was observed by SEM (scanning electron microscope) pictures using a JEOL scanning electron microscope, model JSM-6480 LV; specific surface area was determined by the BET (Brunauer–Emmett–Teller) method following the standard ISO 9277 (2010) (E) on a Quantachrome Nova 1200 instrument.

2.4. Batch adsorption experiments

The adsorption properties of As(III) on Chi-g-AN-C were estimated with sodium arsenite ($NaAsO_2$). An amount of Chi-g-AN-C flakes of 3 g was shaken with 200 ml of $NaAsO_2$ solution in the range of concentration from 0.5 to 5 mmol/l of $NaAsO_2$ or from 65 to 650 mg/l of As(III) for 24 h. The adsorbent was removed by filtration. The equilibrated arsenic concentration was quantified by means of a Perkins-Elmer 5300DV inductively coupled plasma atomic emission spectroscope (ICP-AES). The Langmuir isotherm equation is expressed as follows (Kamari and Wan Ngah, 2009):

$$Ce/Ye = 1/Qb + Ce/Q \quad (3)$$

where Ce is the concentration of As(III) after adsorption (mg/l), Ye is the capacity of As(III) adsorbed (mg/g), Q is maximum adsorption capacity (mg/g) and b is the Langmuir constant (l/mg).

All collected data were expressed as mean ± SE – standard error, in this study. The differences between sample values were assessed using two-tailed unpaired Student's t-tests. The standard error should be $< \pm 5\%$ at a 95% confidence level, and number of samples analyzed per condition is three ($N=3$).

2.5. Continuous adsorption experiments

Adams and Bohart describe the relationship between C_t/C_o and t in a continuous system (Sharma and Singh, 2013). It is used to predict the breakthrough curves for modified chitin column design.

A Shengbo-G_3 column (Zhejiang, China) with an internal diameter of 3 cm with flow rate of 5 ml/min was used for continuous adsorption experiment. In order to investigate the effect of bed height on removal efficiency of As(III) ions, depths of Chi-g-AN-C packed column 10, 20 and 30 cm (equivalent to, respectively, 2.846, 5.538 and 7.923 g) were used for adsorption of As(III) ions at concentration of 75 mg/l. Effluent samples from column were collected at specified time interval of 30 min, and the As(III) concentrations in the effluent were measured by ICP-AES. In all experiments, the temperature and pH values were adjusted to 30 °C and 6.5, respectively.

Adsorption of arsenic from groundwater samples with the depth of about 30 m was also determined. One liter of groundwater sample was flowed through the Chi-g-AN-C packed column from the top to the bottom with a column height of 30 cm. The concentration of arsenic was measured before and after flowing through the column.