Wastewater treatment with chitosan

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Abstract

What does wastewater treatment exactly mean? Water produced by different domestic and industrial activities is known as wastewater. It contains various inorganic, organic and biological contaminants that are of environmental significance. These contaminants can create order and health hazards if discharged into streams or oceans without proper care and treatment.

Chitin, the second-most abundant biopolymer, and its deacetylated product, chitosan, are high molecular-weight biopolymers and are recognized as versatile, environmentally friendly raw materials. Chitosan treatment with citric acid or sulfuric acid produced regenerated chitosans. There are many applications for these chitinous materials including use in agriculture, food processing, medicine, cosmetics, and biotechnology.

The textile industry uses large amounts of water for dying and washing. Textile wastewater is generally alkaline and high in pigments, BOD and suspended solids. The decolorization by chitosan which is decrystallized by citric acid is efficient, fast, and cost effective, and appears to be a promising method for the treatment of alkaline effluent from textile industry containing mixed dye. The decrystallized chitosan with low crystallinity has a high binding capacity for dyes probably due to the high penetration of the dyes into its structure.

The dairy wastewater usually has a high initial pH and a high buffer capacity. When a treatment process should be conducted at pH values as low as 4.3, the consumption of pH-adjusting chemicals dramatically increases together with their cost. Chitosan, a biological cationic polymer, can treat dairy wastewater at pH values up to 5.25 by coagulation. Treatment efficiencies vary with the quality of wastewater, but the results with chitosan indicate a nearly 60% removal of phosphates and COD and over 90% removal of particles. Chitosan can efficiently function at pH ranges even as high as 5.25, while other commercial polymers functioned only at pH below 4.5. The full-scale references indicate that the CMC process functions only at pH<4.3.

Key word: chitosan, waste water, BOD, COD.

Introduction

Do you know what happens to your wastewater after you take a shower, wash the dishes, or flush the toilet? Where exactly does it go? What is in it? How does it affect the environment? And why should you care?

If you are like most people, you never give much thought to what happens to the wastewater from your home and community. But whether you think about it much or not, wastewater continues to affect your life even after it disappears down the drain.

These pictures are very interesting. I believe if you see red soil in the creek, you may be afraid of it, because it is polluted. But the river in this picture, the city, is very clean. And you can see people are happily fishing. Would you
want to join them? And the stream in this picture in the nature is so beautiful. You want to enjoy the beauty of the nature forever, and protect the water resource. So this is what wastewater treatment does, and wastewater treatment is very important.

**Definition of wastewater**

What does wastewater treatment exactly mean?

Water produced by different domestic and industrial activities is known as wastewater. (Mamta, 1999)

It contains various inorganic, organic and biological contaminants that are of environmental significance. These contaminants can create order and health hazards if discharged without proper care and treatment into streams or oceans. (Mamta, 1999)

Contaminations of wastewater includes Chemical-organic, Chemical-inorganic, Biological, and physical. The source of chemical-organic pollutants includes trace organic, biodegradable, floating material. The source of chemical-inorganic pollutants includes nutrients, trace metals, gaseous inorganic. The source of biological pollutants includes pathogenic bacteria. The source of physical pollutants includes suspended solids, dissolved solids. (Mamta, 1999)

**Source of the Chitin and chitosan**

Chitin, the second-most abundant biopolymer, and its deacetylated product, chitosan, are high molecular-weight biopolymers and are recognized as versatile, environmentally friendly raw materials. (Sandford, 1989) The chitin is the major component in the shell of the shrimps, and crabs, cartilage of the squid, and outer cover of insects. Nowadays, there have been several studies on shrimps or crabs chitin, which will provide us a good start of our discussion today on wastewater treatment. (Kim, et al., 1997, No, et al., 2000, Knorr, 1983)

**Prepare of the chitin, chitosan and regenerated chitosan**

Chitin prepared from shrimp waste was treated with 0.5 N NaOH at ambient temperatures to hydrolyze the surface flesh. The alkali-treated waste was washed, then dried and disintegrated to obtain powder. The powder was passed through sieves of 40–60 mesh. The flake-free powder was soaked in 2 N HCl for 2 h to remove minerals until CO2 evolution ceased. The demineralized powder was soaked in 2 N NaOH at 80 C to hydrolyze the protein; then it was washed with water until neutral. The alkali-treated powder was soaked in 1% KMnO4 at room temperature for 1 h to oxidize the astaxanthin, then soaked in 1% oxalic acid at 60 C for 1 h to neutralize the KMnO4. The product was then washed and dried to obtain a white chitin powder. Chitin powder was alkali treated (50% NaOH) at different temperature and different times to obtain chitosans of different degrees of deacetylation. These were washed and dried at 50°C to obtain the final chitosan products. (Chen, 1998) Chitosan treatment with citric acid or sulfuric acid produced regenerated chitosans. (Trung, 2003)

**Structure of the Chitin and Chitosan**

Chitosan is obtained from N-deacetylation of chitin. Both these polysaccharides are copolymers of β-(1-4) linked N-acetyl-D-glucosamine and D-glucosamine units. The degree of acetylation (DA) represents the proportion of N-acetyl-D-glucosamine units with respect to the total number of units. It allows us to define the two terms chitin and chitosan. Thus, in the case of chitosan, DA is considered to be below 50%. This value also determines the solubility limit of the polymer in dilute acidic solutions with it pH value between 2<pH<6. There are many applications for these chitinous materials including use in agriculture, food processing, medicine, cosmetics, wastewater treatment and biotechnology. (Tokura,1995, Stevens, 2001)
Extensive application of chitosan

There are three reasons for the “Extensive application of chitosan. (1) Chitin, the second-most abundant biopolymer and in a large amount. (陳與金，1995) (2) Due to its biocompatibility, biodegradability and bioactivity, it is more and more considered as a very interesting substance for diverse applications as a biomaterial. (Muzzarelli，1977) (3) Chitosan behaves as a polycationic electrolyte in acidic solution, which means a highly cationic charged in acid solution. (Chen & Chen，1998)

Results

Applications of textile wastewater

The textile industry uses large amounts of water for dying and washing. Textile wastewater is generally alkaline and high in pigments, BOD and suspended solids. (Nemerow & Agardy, 1998)

1. Effect of the absorbance values

These spectra of the raw mixed textile dye effluent before and after the decolorization by activated carbon, chitosan and CDC. The CDC obtained from chitosan with 87% DD and 1.12 million daltons was used to test its decolorization capacity for textile wastewater. The results are given in Fig. 1. The decolorization ability of untreated sample is the worst, the next is that of with the activated carbon, then the chitosan. The decolorization ability of CDC treatment is the best. The absorbance values of the textile effluent decreased over the whole range of the visible spectrum. (Trung, 2003)

![Fig. 1. Spectra of the raw mixed textile dye effluent before and after decolorization by activated carbon, chitosan and CDC.]

2. Effect of the content time

For study of absorption of kinetics of CDC for model dye, the orange II, and a series of contact time experiments was carried out at the dye concentration of 10 mg/l. The difference in absorption kinetics of chitosan and the decrystallized chitosan is presented in the figure 7. The result shows that for the decrystallized chitosan, the contact time necessary to reach equilibrium at pH 5.5 is very short, only 10 min, but for normal chitosan was 20 min. (Trung, 2003)

Results in Fig.2. shown that the rate of decolorization of the dye effluent by CDC was faster than that of chitosan and activated carbon. (Trung, 2003)
3. Effect of the pH

Results in Fig. 3. show that using orange II to investigated the effect of pH on the adsorption of anionic dye by chitosan and decrystallized chitosan. The data indicates that the adsorption capacity of the dye by chitosan is strongly dependent on pH and the dye binding capacity of chitosan declines significantly when the pH increases. While the dye binding capacity of CDC was not significantly dependent on pH. CDC had significantly higher dye binding capacity at high pH than chitosan. The high dye binding capacity of CDC was observed over a pH range from 4.5 to 8.5. (Trung, 2003)

Results are in Fig. 4. show the affect of pH of the dye effluent on the decolorization capacity by activated carbon, Chitosan and CDC. The decolorization by activated carbon was low and showed no pH effect. The decolorization capacity of chitosan was depended, and declined when pH increased. This is because less amino groups are
protonated to bind anionic compounds. Konnr (1983) and Kim et al., (1997) also reported a decline in the dye binding capacity of chitoan with a pH range from 4 to 7. At basic pH, amino groups are not charged. At that pH, only physical adsorption occurs. CDC shows a high decolorization capacity even at high pH due to its amorphous state, which is more suitable for physical adsorption. A significant advantage of CDC over chitosan is that it can work efficiently over a pH range from 4.5 to 8.1. (Trung, 2003)

![Fig. 4. Adsorption capacity for anionic dye orange II of chitosan and citric decrystallized chitosan at different pH.](image)

**Fig. 4.** Adsorption capacity for anionic dye orange II of chitosan and citric decrystallized chitosan at different pH.

![Fig.5. Effect of pH the dye effluent on the decolorization by activated carbon, Chitosan and CDC.](image)

**Fig.5.** Effect of pH the dye effluent on the decolorization by activated carbon, Chitosan and CDC.

4. **Effect of the Temperature**

For study of absorption kinetics of CDC for model dye, the orange II was chosen as a model dye and a series of contact time experiments was carried out with the dye concentration of 10 mg/l.

The difference in absorption kinetics of chitosan and the decrystallized chitosan is shown in the Fig.6. The result shows that for the decrystallized chitosan, the contact time necessary to reach equilibrium at pH 5.5, is very short,
only 10 min, but for normal chitosan is 20 min.

Fig. 6. show the effect of temperature of the dye effluent on the decolorization by activated carbon, chitosan and CDC. The dye adsorption capacity reduced when the temperature increase from 25 to 55°C for the CDC. However, for the chitosan, dye adsorption increased slightly at the range from 35 to 45°C and reduced at 55°C. The activated carbon showed higher dye binding capacity at high temperature. So dye adsorption of CDC was more efficient at lower solution temperature in contrary to activated carbon. The CDC and chitosan reduced the adsorption capacity at high temperature. This might be due to the enhancement of desorption at high temperature. (Trung, 2003)

![Graph showing effect of temperature on decolorization](image)

Fig. 6. Effect of temperature of the dye effluent on the decolorization by activated carbon, chitosan and CDC.

5. Characteristics of the Citric acid decrystallized chitosan

Fig. 7. is the x-ray diffraction patterns of original and CDC prepared from various DD or Mw chitosans. Chitosans after decrystallization by citric acid treatment resulted in low crystalline. The original chitosan have sharp x-ray peaks that indicate the high crystalline while CDC having broad x-ray peaks indicated the low crystalline. Chitosans with various DD and Mw can be decrystallized by citric acid. The low crystalline of CDC chitosan samples may be attributed to dissolution of chitosan, the citrate can complex with the NH3. In case of weaker acids tested above need a higher pH for dissociation but at that time the chitosan does not have sufficient protonated groups any longer so the chitosan precipitates. (Trung, 2003)
Conclusion

1. The decolorization by chitosan which is decrystallized by citric acid is efficient, fast, and cost effective, and appears to be a promising method for the treatment of alkaline effluent from textile industry containing mixed dye.

2. The decrystallized chitosan with low crystallinity has a high binding capacity for dyes probably due to the high penetration of the dyes into its structure.

3. The efficiency of decrystallized chitosan for dye binding at basic pH is a very important characterics because it allows the application of this polymer at a pH where normal chitosan can not work efficiently.

4. Chitosan, a biological cationic polymer, can treat dairy wastewater at pH values up to 5.25 by coagulation. Treatment efficiencies vary with the quality of wastewater, but the results with chitosan indicate a nearly 60% removal of phosphates and COD and over 90% removal of particles.

5. Chitosan can efficiently function at pH ranges even as high as 5.25, while other commerical polymers functioned only at pH below 4.5. The full-scale references indicate that the CMC process functions only at pH<4.3.

References


