

## A filtration water treatment device for colored waste water treatment

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**Abstract:** *The designs of technological small water water treatment sorption devices loaded with magnetic chitosan microspheres have been researched. In addition, their applications in the wastewater treatment, based on different kinds of colored wastewater, have been tested, and their technological behaviour during the process of dye removal have been discussed.*

**Key words:** *magnetic chitosan microspheres, small water treatment device, applications in colored wastewater treatment*

### INTRODUCTION

Water is one of the most basic requirements for human daily life. However, with rapid development of modern industries, the problem of water pollution turned more serious day by day, on the other hand, the higher quality of water has been demanded with increasingly stringent environmental quality standards. In the view of the characteristics of current water pollution, the quantities of soluble organic compounds and nonbiodegradable matters increased rapidly in water, but, the conventional technologies of wastewater treatment were not efficient for removal of these impurities. Furthermore, some toxic residue in water may be produced by many currently used reagents for water treatment, which were very disadvantageous for the human health (mainly halogen derivatives) and environment. Therefore, it was one of the hottest research projects in the field of the wastewater treatment to search the new technologies and designs with the characteristics of high efficiency, low cost and nontoxicity. Many industries, such as textile, paper, plastics and dyestuffs, consume substantial volume of water, and also use chemicals during manufacturing and dyes to color their products. As a result, they generate a considerable amount of polluted wastewater [1–5]. For example, pulp and paper mills generate varieties of pollutants depending upon the type of the pulping process. Their toxic effluents are a major source of aquatic pollution and will cause considerable damage to the receiving waters if discharged untreated [1]. This specific type of pollution is characterized by high biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (mainly fibers), bad smell, toxicity (high concentration of nutrients, presence of chlorinated phenolic compounds, sulfur and lignin derivatives, etc.), and especially color [1,2]. Color is the first contaminant to be recognized in wastewater and the presence of very small amounts of dyes in water is highly visible and undesirable [4,5]. It is now recognized that adsorption using low-cost adsorbents is an effective and economic method for water decontamination. A large variety of non-conventional adsorbents materials have been proposed and studied for their ability to remove dyes [6-8]. However, low-cost adsorbents with high adsorption capacities are still under development to reduce the adsorbent dose and minimize disposal problems. Much attention has recently been focused on various biosorbent materials such as fungal or bacterial biomass and biopolymers that can be obtained in large quantities and that are harmless to nature. Special attention has been given to polysaccharides such as chitosan, a natural aminopolymer. It is clear from the literature that the biosorption of dyes using chitosan is one of the more frequently reported emerging methods for the removal of pollutants. Natural polymer materials, coming from animals, plants, microorganisms and so on, are a kind of resources abundant in nature, which, after being disused, are facile to degrade into water, carbon dioxide and so on, and they are believed to be nontoxic and environment-friendly materials. Furthermore, what is most important is that natural polymers are also a kind of reproducible and inexhaustible materials fully independent of petroleum resources. Those peculiarities of natural polymer materials have been already applied widely into different fields such as biotechnology, biomedicine, food, and cosmetics [9]. However, in the field of water treatment, natural polymers have also shown excellent performances for distributing abundant free hydroxyl, amino and other

active functional groups on the chain backbone, and natural polymer materials have already been believed to be one of the best substitutes applied in water treatment.

Chitosan, poly- $\beta$ -( $\rightarrow$  4)-2-amino-2-deoxy-D-glucose, is one of the high performance polysaccharide materials, which is prepared from deacetylation of natural chitin, and chitin is the second most abundant natural polymers in the world. In addition, chitosan has many prominent characteristics such as low toxicity and high biocompatibility. so it has been already widely applied in many fields. Furthermore, chitosan presented abundant free amino groups along the chain backbone that are cationically charged in a wide range of physiological pH, and showed prominent flocculating effect. On the other hand, chitosan still bears excellent chelating effect on the abundant free -OH and -NH<sub>2</sub> groups, and could carry out efficiently removal of metal ions, humic acids and synthetical surfactants for formation of complex precipitation. In addition, chitosan could be also used as adsorbent to adsorb impurities from the water. Therefore, it was believed that chitosan is very useful and powerful in the field of wastewater treatment because of its multifunction: flocculating, chelating and adsorption effects.

### EXPERIMENTAL

Chitosan is usually used in a flaked or powdered form that is both soluble in acidic media and nonporous. Moreover, the low internal surface area of the nonporous polymer limits access to interior adsorption sites and hence lowers dye adsorption capacities and adsorption rates. To overcome this obstacle, porous beads were synthesized. Indeed an interesting characteristic of the chitosan is its excellent ability to be processed into porous structures. Actually, to obtain a chitosan as a substance to be granulate and tested we use different kind of raw natural materials from Black Sea beach areas (crab shell, shrimp shell). At very first they were crushed and pulverized in a ball mill device and the powder was screened through a 60-mesh sieve. The screened powder obtained was used for our next conditioning procedures. Hydrogen peroxide, acetic acid and sodium hydroxide were purchased from Bourgas Commers Company (Bourgas 8000, Bulgaria). All chemicals were of analytical grade. The succession of next procedures were as follows:

- Extraction of chitin from shrimp shell [10]

Diluted HCl solution was used for demineralization (removing of calcium and other carbonates from the shell structure). One hundred grams of shrimp shell powder was immersed in 1000 ml of 7% (w/w) HCl at room temperature (25 °C) for 24 h. After filtration with midspeed filter paper, the residue was washed with deionized water to neutral. Then the residue was immersed in 1000 ml of 10% (w/w) NaOH at 60 °C for 24 h for deproteination. The proteins were removed by filtration. Deionized water was used to wash the residue to neutral. Then the shrimp shell residue was subjected to the above program for two times. 250 ml of 95% and absolute ethanol were sequentially used to remove ethanol-soluble substances from the obtained crude chitin and to dehydrate. An air oven was taken to dry the chitin at 50 °C overnight.

- Preparation of chitosan

The chitin (20 g) was put into 50% NaOH at 60 °C for 8 h to prepare crude chitosan. After filtration, the residue was washed with hot deionized water at 60 °C for three times. The crude chitosan (7.5g) was obtained by drying in an air oven at 50 °C overnight. One gram of crude chitosan was added into 20 ml of 2% (w/w) acetic acid in a water-bath shaker. The conditions were set as follows: H<sub>2</sub>O<sub>2</sub> level (4–6%), time (2–4 h) and temperature (20–60 °C). After reaction, 10% NaOH was used to adjust the solution to neutrality. The residue was removed by filtration, while two fold volumes of ethanol were added to the filtrate. The crystal of water-soluble chitosan was liberated after incubation at ambient condition overnight and dried in an air oven at 50 °C. The recovery (%) was calculated as (the weight of water-soluble chitosan / the weight of crude chitosan) × 100.

- Preparation of magnetic chitosan microspheres

As known, chitosan was a kind of natural organic polymer materials, and usually immiscible with inorganic matters. Therefore, it was difficult to disperse the inorganic magnetic particles into organic polymers homogeneously for preparation of the high-performance inorganic-organic composites. In addition, the structure of chitosan chain was stiff, and chitosan could dissolve in very few solvents, usually only in acidic aqueous media. Based on these characteristics of chitosan, two methods for preparation of magnetic chitosan microspheres (MCM) have been summarized: reverse-phase suspension cross-linking and precipitation method. To form magnetic chitosan particle reverse-phase suspension cross-linking method (RPSCLM) [11] was used. For RPSCLM, firstly, a stock solution of chitosan was freshly prepared by dissolving in acidic aqueous solution. Secondly, magnetic particles have been dispersed into the chitosan solution; then, the organic solvent, such as paraffin, was added into the mixture to form a water-in-oil reverse-phase suspension; at last, the microspheres have been chemically cross-linked usually by formaldehyde and glutaraldehyde. Because of bad miscibility between inorganic and organic compounds made it quite difficult to disperse the magnetic particles into the polymer solution homogeneously. For mixing well the two immiscible compounds, two popular methods have been applied: one was to add the inorganic particles into the prepared polymer solution directly, and the magnetic particles were dispersed by physical methods such as ultrasonic treatment and mechanical stirring; the other was to disperse and stabilize the magnetic particles in the aqueous solution by emulsification firstly, then the above prepared magnetic fluid was added into polymer solution for mixing. For getting high magnetic quality for the MCM, the magnetic particle / chitosan mass ratio was a key parameter. It is indicated [12] that the chitosan-Fe<sub>3</sub>O<sub>4</sub> magnetic microspheres would have efficient effect of magnetic separation, when the Fe<sub>3</sub>O<sub>4</sub>/ chitosan mass ratio is higher than 9.05%.

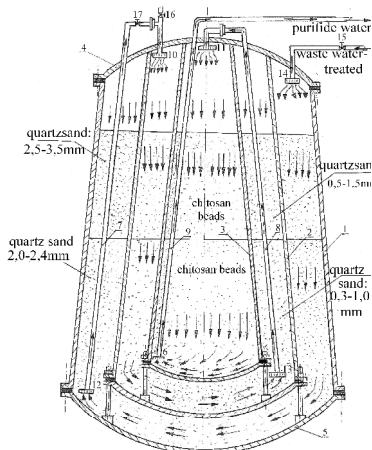
Really, the properties of MCM prepared by RPSCLM, such as the size/distribution, and magnetic quality, have been greatly affected by the different experimental parameters, such as the magnetic particle / chitosan mass ratio, concentration of chitosan, reaction time, stirring rate, and the water/oil ratio. It was found that the size of the MCM by RPSCLM decreased with increasing Fe<sub>3</sub>O<sub>4</sub> contents, implying that dispersion of chitosan solution into microspheres was more difficult when the Fe<sub>3</sub>O<sub>4</sub>/chitosan mass ratio increased. The stirring rate of the suspension medium was another effective parameter for the properties of the microspheres. With the stirring rate increase, the size of microspheres decreased, which was ascribed to the increase of the energy transferred to the suspension medium, and made the polymer solution be dispersed into smaller droplets and size was reduced. In addition, it was found that the molecular weight of chitosan had no significant effect on the properties of MCM in their given molecular weight range. The concentration of chitosan was also very important for the formation of microspheres. If the concentration of chitosan was high, the viscosity of polymer solution was increased, which made it difficult for the magnetic particles to be dispersed efficiently, and the size of the microspheres also increased.

After the magnetic chitosan microspheres were obtained, they were loaded into a filtration multi cell small water treatment device (fig.1). We created this pilot device to use it at some multi process filtration experiments (process for removing the mechanical insoluble dispersed impurities from the water; adsorption process for removing dye, heavy metals; ion-exchange processes etc.). The experiment show that our multi cell device is able to possess a multifunction ability just in one body (fig.1), depending on the filtration materials loaded there.

## RESULTS AND DISCUSSION

The effectiveness of chitosan for its ability to interact with dyes has been studied by numerous workers. Juang and co-workers [13–17] demonstrated the usefulness of chitosan for the removal of reactive dyes. We found also that the maximum adsorption

capacities of chitosan for dyes: RR 222, RB 222 and RY 145 were 1482, 969 and 832 mg/g adsorbent, respectively. Our results confirm the research information given by different authors. Annadurai [18,19] and Crini et al. [19] also reported that chitosan may be a useful adsorbent for the effluent of textile mills because of its high adsorption capacity. Uzun and Guezal [21–23] noted that chitosan can be used in the studies of dyestuff adsorption in comparison with most other adsorbents.



**Fig. 1.** Multi cell multi process small water treatment: 1-outside body;2-interside body;3- inside body;4-upper cover; 5-bottom cover; 6,10,11,12,13,14-nozzles; 7,8,9-communication pipes ;15,16,17-valves (Zvezdov, A., Pat. BG 51392 A B 01 J 47/02,1996); ;( Zvezdov, A., Pat. BG 234 Y 1 C 02 F 1/42)

This polysaccharide showed a higher capacity for adsorption of dyes than CAC and other low-cost adsorbents, as reviewed by Crini [6]. Kim and Cho [11] also indicated that the amount of RB 5 adsorbed on chitosan beads is much greater than on CAC. Similar conclusions were reached by Lima et al. [24] for the BB 9 adsorption. McKay's group [25–27] recently published a series of papers on the ability of chitosan to act as an effective adsorbent for the removal of acid dyestuffs from aqueous solution. The monolayer adsorption (saturation) capacities were determined to be 973.3, 922.9, 728.2 and 693.2 mg of dye per gram of chitosan for dyes: AO 12, AO 10, AR 73 and AR 18, respectively. The interaction between chitosan and anionic dyes has also been intensively investigated by Guibal and co-workers [28–31]. Their and our investigations clearly indicated that chitosan had a natural selectivity for dye molecules and was very useful for the treatment of wastewater. They reported that adsorption capacities ranged between 200 and 2000 mmol/g for chitosan and significant lower (between 50 and 900 mmol/g) for CAC.

## CONCLUSION

On the base of published information and our experimental results, we concluded that chitosan exhibited a twofold or more increase in the adsorption capacity compared to CAC in the case of acid, direct, reactive and mordant dyes. The best choice for the adsorbent between CAC and chitosan depends on the dye, however, it was impossible to determine a correlation between the chemical structure of the dye and its affinity for either carbon or chitosan. It is evident from the brief literature survey and the results obtained that the granulated chitosan can be utilized as an interesting adsorption material to be

loaded in filtration devices for the purification of dye-containing wastewater because of its outstanding adsorption capacity.

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**Докладът е рецензиран.**