Chitosan – A Natural Adsorbent for Copper Ions

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Abstract - As a result of industrial activities and technological changes, a high and continuously increasing amount of heavy metals and heavy metal containing effluents are released into the environment by different industrial nations. These metals cannot be degraded. Furthermore, because of their toxicity, they are highly detrimental to the environment and human health. Heavy metals accumulate in the food chain and become permanent pollutants in the environment. In the human body they accumulate in different organs causing serious damage.
    To overcome this problem, the adsorption behaviour of heavy metal ions, in particular copper ions was investigated by apply chitosan flakes, powder, and beads as a natural adsorbent. Metal removal was studied using adsorbance measurements, SEM-EDX, and size measurements. The adsorption capacity of chitosan was determined at different concentration and times. The received adsorption capacities for copper ions were very promising, with a maximum value of 150 mg/g on chitosan powder.

Keywords: chitosan, removal, heavy metal ion, adsorption, waste water treatment

1. Introduction

Waste water treatment, sludge dewatering, pulp and paper production are typical examples for solid-liquid separation through coagulation and flocculation. The overwhelming majority of these processes uses polyelectrolytes to regulate the stability and flocculation properties of the disperse systems. This resulted in a great variety of synthetic and natural flocculants like chitosan and starch as natural products which are now commercially available to meet the specific demands of industrial fields, where an efficient solid-liquid separation is required [1-7]. The removal of inorganic components/particles has been intensively investigated during the last years. Hence, it is much more difficult to remove soluble components like dye [8, 9], surfactants, or metal ions. This work will focus on the separation of heavy metal ions especially copper ions with chitosan as a natural polymer.

Heavy metal processing industry has always been a major of concern which affect surface water, drinking waters, ground waters, and rivers contamination. With the agreement to comply limiting values (according to the precautionary principle) [10] as they can be found in the European drinking water directive, the non-damaging of human health at lifelong consumption will be ensured. Actual limiting value of the German drinking water directive of copper ions is 2 mg/L [11].

Besides the endangerment for the environment and human health, heavy metal containing effluents are a source of potentially regenerative materials. The separation and recuperation of heavy metals from the material flow is ecologically and economically required. Thus, the implication is to design efficient and effective strategies to recycle and recover heavy metal ions from industrial effluents [12, 13]. The intention of this study is the development of a process, which can be used to separate heavy metals in a selective manner from the effluents, especially at low concentrations. The separation is supposed to be accomplished with the help of polyelectrolytes. Since several decades, researches carried out a method of separating heavy metals from effluents by using polyelectrolytes. In 1996, it was shown within an ultra-filtration experiment that polyelectrolytes are promising substances to remove traces of heavy metals from industrial effluents [14]. Furthermore, it was proved that remaining amount of heavy metal in decontaminated water could significantly be reduced by application of polymeric flocculants, in comparison to inorganic flocculants [15].

Chitosan is a natural polymer and prepared by the deacetylation of chitin. The degree of deacetylation reclines between 50 and 100%. The good adsorption properties of chitosan on heavy metal ions has long been known and is mainly

attributed to the presence of the so formed secondary amino groups which occur both charged or uncharged depending on the pH of the solution. So far, various articles have been published focussing on the removal of watersoluble impurities especially heavy metal ions using polyelectrolytes like poly(acrylic acid) and poly(ethylene imine), or chitosan as a soluble flocculation or chelating agent [15]. In this work, we focused on the removal of copper ions by using defined chitosan flakes, powder, and beads as efficient adsorber material.

2. Experimental

Chitosan was purchased from BioLog GmbH. The degree of deacetylation (DA) reclines between 85 and 90% for the investigated samples displayed in Table 1:

Table 1: Properties of the investigated chitosan samples, DA – degree of deacetylation.

Sample Name	Da	Molar Mass	Ash Content
Ch90/200/A1	90 %	200,000 g/mol	< 1%
Ch85/400/A2	85 %	400,000 g/mol	< 2%

The investigated Chitosan materials differed in their degree of deacetylation, particle size, and morphology (i.e. flakes, powder, or beads). The flakes have a wide particle size distribution in the mm range. With laser diffraction we determined a particle size distribution of the powder with a D 50 value of 200 µm. The beads had a diameter of about 3 mm in the swollen state.

The adsorption capacities were determined in dependence on the initial concentration of copper ions in solution, as well as on the time of adsorption (contact time between adsorbent and adsorbate). Copper sulfate pentahydrate was utilized for all experiments. The adsorption investigations were carried out as batch experiments. Adsorption capacities were calculated by adsorbance measurements. For every experiment, the concentration of copper ions was measured before and after the adsorption procedure at a defined time.

3. Results and Discussion

Contact time is a very important parameter for adsorption experiments, the adsorption capacity calculated later on at a certain time, and for a useful application. Figure 1 shows the increasing amount of copper ions adsorbed on chitosan as a function of time. The maximum adsorption uptake has been reached after 24 h for all samples. Therefore, for calculating the adsorption capacities all batch experiments were carried out after 24 hours adsorption when equilibrium was reached. Almost 100 % of the copper ions were removed from water after 24 hours for an initial copper concentration of 180 mg/L. Furthermore, after 1 hour adsorption time 60 % of the copper ions were adsorbed in chitosan already.

Fig. 1: Adsorbed copper ions on chitosan flakes Ch90/200/A1 in dependence on time with an initial copper concentration (C_{Cu2+}) of 180 mg/L.

Chitosan is a white material which changes its colour during the adsorption of heavy metal ions in aqueous solution towards the colour of the adsorbed metal salt (see Figure 2). The colour intensity depends on the initial concentration of the heavy metal salt as well as on the adsorption time. (Copper sulfate is a grey white solid which appears in a beautiful blue colour as shown in Figure 2 in its hydrated form.) The color change of the material gives evidence of the adsorption of copper ions. Furthermore, the adsorbents were characterized be SEM-EDX measurements before and after adsorption process (here not shown). The SEM-EDX measurements indicated an adsorption of copper ions as well as sulfate ions.
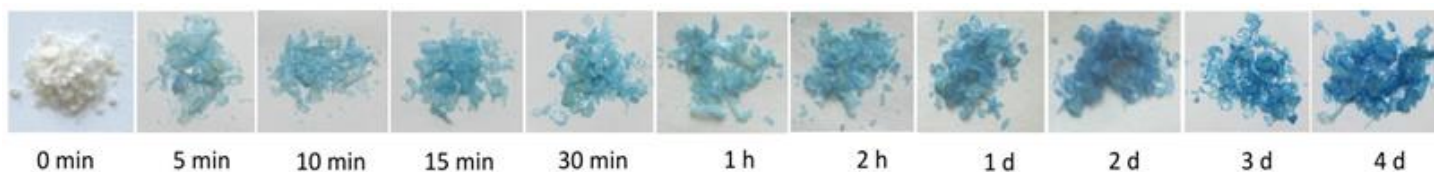

Fig. 2: images of chitosan flakes Ch90/200/A1 in dependence of the adsorption time and as a result the increasing color intensity of chitosan due to the increasing adsorption of copper sulfate.

Fig. 4: Adsorption capacity of different types of chitosan materials in dependence of the initial copper ion concentration, adsorption time of 24 h.

In Figure 4 the adsorption capacity of the different types of chitosan in dependence of the initial Cu^{2+} concentration is shown. The adsorption capacity is the difference between the initial concentration of the metal ion and the metal ion concentration after adsorption multiplied by the volume used, and divided by the mass of the adsorbent. The pH of the solutions was not adjusted. The adsorption capacities differ significantly from each other in the range powder >flakes>beads. In general, three different adsorption capacities could be obtained depending on the morphology of the material. The highest adsorption capacity was achieved with the chitosan powder. As the powder had the lowest particle size of all the examined materials, the surface area will be the highest. Hence, the higher the surface area, the higher will be the theoretical adsorption capacity. Therefore, the observed values in Figure 4 show a strong dependence on the surface area, thus with the type of chitosan material used. The adsorption capacities of the chitosan flakes with 85 and 90 % degree of deacetylation do not differ significantly. The reason could be the small difference in the degree of deacetylation. Hence, the adsorption capacity does also depend on the accessibility of the available amino groups. Furthermore, the analyzed chitosan beads are coated alginate beads with a small layer of chitosan on top of it. Therefore, the beads are difficult for comparison with the other three chitosan materials due to the possible different chemical moieties on the surface, as the amino groups might stick to the alginate surface. This could be another reason for the low adsorption capacities on the beads. Investigation on studying the dependence of DA and molar mass for the adsorption properties are in progress.

The achieved adsorption capacities for copper adsorption on chitosan are very high in comparison to other adsorbents, independent on the morphology of chitosan. Activated carbon functionalized with secundary amino groups exhibited an adsorption capacity of 140 mg/g for copper ions [16]. Other non-natural polymers (e.g. resins and carbamates) possessed adsorption capacities between 80 and 70 mg/g [17, 18, and 19]. Hence, one should note that the adsorption capacities of different types of materials were compared without any additional information to it. In this publication the achieved adsorption capacities of one material with different morphologies was examined and compared. The morphology is one of a number of parameters that are dependent for the adsorption capacities.

4. Conclusion

In principle chitosan is a suitable adsorbent for heavy metal ions in aqueous solution. The highest adsorption capacity was achieved for chitosan powder because of the high accessible surface for metal ions. Chitosan beads have much lower adsorption capacities than the chitosan flakes and powder probably due to the small amount of chitosan that was coated on the surface of the alginate beads. It was found that during the adsorption process metal cations as well as the anions of the used salts adsorb on chitosan surface. In dependence on adsorption time and initial salt concentration the formation of crystal-like structures was observed. Hence, the type of the anion might also have a distinct influence on the adsorption capacity.

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