

Adsorption of Cu(II) and Cr(VI) ions by chitosan: Kinetics and equilibrium studies

R Schmuhl, HM Krieg and K Keizer*

School for Chemistry and Biochemistry, Potchefstroom University for Christian Higher Education, Potchefstroom 2531, South Africa

Abstract

The ability of chitosan as an adsorbent for Cu (II) and Cr (VI) ions in aqueous solution was studied. The experiments were done as batch processes. Equilibrium studies were done on both cross-linked and non-cross-linked chitosan for both metals. Cr (VI) adsorption behaviour could be described using the Langmuir isotherm over the whole concentration range of 10 to 1000 mg·l⁻¹ Cr. The maximum adsorption capacity for both types of chitosan was found to be 78 mg·g⁻¹ for the non-cross-linked chitosan and 50 mg·g⁻¹ for the cross-linked chitosan for the Cr (VI) removal. For the Cu (II) removal the Freundlich isotherm described the experimental data over the whole concentration range of 10 to 1000 mg·l⁻¹ Cu (II). The maximum adsorption capacity for both types of chitosan can be estimated to be greater than 80 mg·g⁻¹. Cr (VI) removal was the highest at pH 5 but pH did not have a large influence on Cu (II). From these results it is clear that the adsorption of heavy metals is possible with chitosan, but that with this method, end concentrations of below 1 mg·l⁻¹ can hardly be obtained.

Introduction

Industrial and mining wastewaters are important sources of pollution of heavy metals (Quek et al., 1998). The use of chromate and dichromate in metal plating and as corrosion control agents in cooling waters is quite extensive. It is well-known that Cr (VI) is toxic to living systems and must be removed from wastewater before it can be discharged. Current treatment for the removal of Cr (VI) involves acid catalysed chemical reduction to Cr³⁺. The Cr³⁺ is then precipitated as hydroxide at alkaline conditions using either caustic or lime (Udaybaskar et al., 1990). The presence of Cu (II) in wastewater is also a problem. Copper is used extensively by electrical industries, in fungicides and in anti-fouling paints. When Cu is ingested at high concentrations it can become toxic to humans, causing cancer and promoting oxidation. The present method for removal of Cu is to precipitate copper hydroxide by liming. But with this process, residual Cu remains a problem (Findon et al., 1993).

Owing to their wide use, the efficient removal of toxic metal ions from wastewater is an important and widely studied research area where a number of technologies have been developed over the years (Deans and Dixon, 1992). The most important of these methods include filtration, chemical precipitation, ion exchange, adsorption, electrodeposition and membrane systems. All these approaches have their inherent advantages and limitations. Although filtration and chemical precipitation are low-cost and effective in removing large quantities of metal ions quickly, neither is capable of removing trace levels of metal ions. Adsorption is also ineffective at very low concentrations of metal ions. Ion exchange can be used to reduce metal concentrations to the region of parts per million. In recent years studies on polymers, which bind metal ions, have increased significantly. Studies on the polymer-metal complexes are of great practical importance. Complexing abilities of polymers are used in nuclear chemistry, electrochemistry, hydrometallurgy

and environmental protection (Kamiński and Modrzejewska, 1997). Of particular significance among many methods of metal-ion separation is the one which combines two processes: complexing of a polymer with metal ions and ultrafiltration of the complexes through membranes of appropriate selectivity (Kamiński and Modrzejewska, 1997).

A technique, which has been widely studied in the laboratory, but not widely applied industrially, is the use of chelation ion exchange. Chelation ion exchange takes advantage of the three-dimensional structure of the molecules to chelate and remove ions of a specific size in the presence of large quantities of other ions (Deans and Dixon, 1992). This approach is inherently attractive since only the toxic metal ions are removed while the harmless ions can be released into the environment. Some of the best chelation ion-exchange materials are biopolymers.

Biopolymers are industrially attractive for a number of reasons; *inter alia*, their capability of lowering transition metal-ion concentration to parts per billion concentrations, they are widely available and are environmentally safe. Such materials include cellulose, alginates, carrageenan, lignins, proteins, chitin and chitin derivatives. Another attractive feature of biopolymers is that they possess a number of different functional groups, such as hydroxyls and amines, to which metal ions can bind either by chemical or by physical adsorption (Deans and Dixon, 1992). Metal removal can be more effective by using chelation ion exchange as a polishing step after the majority of the metal ions have been removed. Since the metals used for chelation ion exchange will tend to have higher associated production costs, it is impractical to use them for removing massive quantities of heavy metals from water. However, it is possible to regenerate them *in situ*, by simply exposing the metal-laden materials to aqueous acid solutions, when desired. This study focuses on chitin derivatives for the removal of heavy metals such as Cr and Cu.

As the degree of deacetylation (DD) of chitinous material exceeds 50%, it becomes soluble in acidic aqueous solutions and is called chitosan (Tsaih and Chen, 1997). The characteristics of chitosan depend on the degree of deacetylation, the distribution of acetyl groups, chain length, and molecular mass distribution.

* To whom all correspondence should be addressed.

☎(018) 299-2359; fax (018) 299-2350; e-mail: chekk@puknet.puk.ac.za
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