

Characterization of Copper Adsorption onto an Alginate Encapsulated Magnetic Sorbent by a Combined FT-IR, XPS, and Mathematical Modeling Study

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Copper adsorption onto calcium alginate encapsulated magnetic sorbent is studied in this paper. The objective of this study was to qualitatively and quantitatively elucidate the copper binding onto the sorbent. The adsorption increases from around 0 to almost 100% as the initial pH is increased from 2 to 5. A maximum adsorption capacity of 0.99 mmol g⁻¹ is achieved. The FT-IR and XPS studies show that the C—O in carboxyl group of alginate directly attaches to the copper ion that leads to most of the adsorption. A mathematical model is developed, and it includes ion exchange between the calcium and the copper, coordination reaction between the functional group and the copper, as well as surface complex formation between the iron oxide and the copper. The model is capable of describing and predicting effects of various key operational parameters on the adsorption process, such as initial pH, metal concentration, and dosage of sorbent.

Introduction

Heavy metal wastes from many industries have adverse effects on our water environment. Adsorption is a cost-effective technology for the decontamination of heavy metals. In recent years, magnetic sorbent has received considerable attention due to ease in separation after usage. Some applications include removal of oil, volatile organic compounds, and heavy metals (1–3). Magnetic iron oxide has been used to fabricate new sorbents together with other functionalized materials such as zeolite, chitosan, and activated carbon (1, 4–6). The resulting sorbents have advantages of high adsorption capacity and ease in separation.

Limited studies are reported on the fabrication of magnetic sorbent for metal removal. In our recent study, an innovative calcium-alginate encapsulated magnetic sorbent was developed for effective removal of copper and arsenic (7). A good understanding of the adsorption mechanism and a successful simulation tool were not obtained. The adsorption mechanisms can be better elucidated via Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and mathematical modeling simulation tools.

FT-IR and XPS provide good insight into adsorption process at the molecular level as reported in the literature (8–11). They have been adopted to identify the major functional groups of adsorbents and elucidate their interactions with metal ions. The possible organic functional groups in the metal binding include carboxyl, ether, alcoholic, hydroxyl, and amino functional groups. Both techniques, however, cannot provide a quantitative description of the sorption process, which is important in the design and engineering of treatment systems. Nonetheless, they are essential to provide evidence to further support the formation of mathematical models.

Metal sorption process is usually described by empirical models (e.g., Langmuir isotherm, and its extended forms) and mechanistic models. The empirical models are able to describe experimental results as a function of metal equilibrium concentration; however, they fail to better predict the effects of such important factors as pH or competitive factors. For example, Jang et al. developed extended Langmuir models to describe metal adsorption onto an alginate gel (12, 13). Good fitting of the experimental data was demonstrated. However, the model parameters were pH-dependent.

Several mechanistic models, such as surface complex formation model (SCFM) (14, 15), and ion exchange model (IEM) (16, 17) are reported in the literature. It is hypothesized that the metal adsorption process is solely controlled by either of them. In SCFM, a weak acidic functional group is often assumed, which leads to the formation of metal complexes. On the other hand, IEM assumes that hydrogen or light metal ions (e.g., calcium), originally present in adsorbent, exchange with heavy metal ions in solution, by which metal ions are removed. Carboxyl groups on biosorbents (e.g., alginate) have a greater capacity for metal binding (8–10, 17–19). Virgin biosorbents normally have higher contents of carboxyl-light metal/hydrogen complexes. When heavy metal ions are present in aqueous solutions, they can be easily removed due to ion exchange reactions between heavy and light metal/hydrogen ions because the affinity of heavy metals for the carboxyl groups is much greater than that of light metal/hydrogen ions. SCFM and IEM work well in metal adsorption onto soil (14–16), and biosorbent (17), respectively. Both models are limited to specific conditions. Modeling of metal sorption onto composites was seldom reported.

In this study, the calcium-alginate encapsulated magnetic sorbent, a composite, has key components of calcium, alginate, and magnetite. Modeling such a complex case has yet to appear in the literature and thus posted a great challenge. Various SCFMs and IEMs have their own application ranges and thus are not suitable for our study. The IEM gives a nice description of metal binding onto the protonated seaweed (17). The model is obviously not suitable as the magnetic sorbent is not protonated and contains calcium and magnetite. The SCFM cannot be used as the sorbent has an ion exchange property. A single model, either SCFM or IEM, cannot predict the adsorption process. There is, therefore, a need to develop one new model to better simulate the process.

The goal of this study was to qualitatively and quantitatively elucidate the copper binding onto the magnetic adsorbent. FT-IR and XPS were employed to identify functional groups and their interactions with the metal ions. A new adsorption model based on a combination of ion exchange and surface complex formation was developed to describe the sorption process. Potentiometric titration and adsorption experiments provided basic characteristics of magnetic adsorption which were used in the determination

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