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 de-
veloped 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 spec-
troscopy (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 interac-
tions 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 equi-
librium 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 demon-
strated. 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 ap-
plication 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 quanti-
tatively 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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