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Low-cost biosorbent: *Anadara inaequivalvis* shells for removal of Pb(II) and Cu(II) from aqueous solution

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ABSTRACT

This study used untreated *Anadara inaequivalvis* shells as a biosorbent for Cu(II) and Pb(II) ion removal from aqueous solutions. The biosorbent was characterized using SEM, XRD, BET, and FT-IR. Results showed that the main seashell structure was aragonite with a heterogenic surface. Batch experiments were performed to determine the effects of contact time, initial pH, and biosorbent amount on biosorption efficiency and the isotherms were examined. The biosorption thermodynamics and kinetics also were determined using equilibrium data. The maximum biosorption capacities of Cu(II) and Pb(II) were 330.2 and 621.1 mg/g, respectively (seashell particle size 250 μm, 100 mg/L metal ion solution, 2.5 mg biosorbent, 25 °C). Langmuir isotherm fitted the equilibrium data better than the Freundlich and Temkin isotherms; biosorption was spontaneous and exothermic. The kinetic parameters were pseudo-second-order. This low cost and natural biosorbent successfully removed heavy metal ions from water and could be used to treat wastewater.

1. Introduction

The development of industrial activities has introduced serious environmental problems. Different forms of pollution have occurred as a result of technological advances and rapid consumption. These forms of pollution have been identified and prevented through the use of various analytical methods. Metals are abundant in the environment; they are also active pollutants (Fu and Wang, 2011). The most common heavy metal contaminants are Cd, Cr, Cu, Hg, Pb, and Zn; of these, Pb and Cu are the most commonly examined in the literature. Lead is ubiquitous in the environment and arises from both nature and anthropogenic sources. Long term drinking water containing high level of lead can cause anemia, brain damage, mental deficiency, anorexia, and the inhibition of enzyme activity (Pehlivan et al., 2009). Low concentrations of Cu are essential and required by the body for enzyme synthesis, and tissue and bone development; however, excess amounts are toxic and carcinogenic, causing stomach and intestinal distress such as nausea, vomiting, diarrhea, and stomach cramps (Akar et al., 2009). Mining operations, fossil fuel combustion, paint and pigments, metallurgical industries, batteries, and pesticides are the main sources of lead and copper metals (Pehlivan et al., 2009). Therefore, the removal of heavy metals from aqueous solution is very important and studies on the topic have increased over recent years.

A number of methods such as precipitation, oxidation/reduction, ion exchange, electrochemical process, etc., have been used to reduce and reclaim heavy metals from aqueous solution; however, these methods are expensive and can cause secondary pollution (Camci-Unal and Pohl, 2010). Adsorption methods are considered suitable for heavy metal removal, due to their utility, practicality, and low cost (depending on the adsorbents used) (Cengiz et al., 2012; Bozbas Karayunlu et al., 2013). Given the important role in heavy metal removal, identifying cheap and readily availablenatural

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adsorbents has attracted growing interest (Ahalya et al., 2003; Cengiz et al., 2012). To date, hundreds of studies on the use of low-cost adsorbents have been conducted (Babel and Kurniawan, 2003; Mohammed et al., 2014).

Biosorbents investigated for sorption have been cheap, environmentally friendly, and abundant biological materials (Köhler et al., 2007), containing different functional groups such as carboxyl, sulfate, phosphate, and amino groups. Many forms of biological materials have been used as biosorbents for heavy metal removal from aqueous solution, such as biomasses like moss (*Hylocomium splendens*) (Sari et al., 2008), nonliving lichen biomass of *Cladonia rangiformis* (Ekmekyapar et al., 2012) and microorganisms (Dursun, 2006), as well as different forms of inexpensive non-living plant material like seeds, peels (Meneghel et al., 2013), and shell materials (Vijayaraghavan et al., 2006; Köhler et al., 2007; Du et al., 2011). Seashell materials in different forms are inexpensive and freely available on sea coasts worldwide. They are also ubiquitous in seafood processing wastes. The use of these seashells as sorbents transforms a potential waste material into a useful resource. Biogenic aragonite and calcite shells are effective for removal of Pb (II), Cd (II), Zn (II) from aqueous solution. Calcite phase of $CaCO_3$ cannot be influent for the removal of Cd (II) in aqueous solution while biogenic aragonite shells may be a way for removal of Cd (II) from wastewater. Du et al. (2011) was mentioned in their study that removal of heavy metals from wastewater can be performed easily by seashells instead of geological $CaCO_3$ and other materials (Du et al., 2011). Some pretreatment processes, such as acid treatment (Niu and Volesky, 2006), thermal processing (Yu and Kaewsarn, 2000), and organic chemicals (Li et al., 2013) can be used to significantly increase the biosorption capacity of shells. Niu and Volesky were performed acid treatment to the crap shells for the biosorption of chromate and vanadate species (Niu and Volesky, 2006). Biomass of *D. potatorum* was heated in an oven at 60 °C for 24 h and used as an efficient biosorbent material for the treatment of Ni^{2+} from aqueous solutions (Yu and Kaewsarn, 2000). With adding organic compound (superabsorbent) to seashell powder and formed a composite solved the recovery problems of seashells (Li et al., 2013). Pyrolyzed outer shell of Horseshoe Crab (*Limulus polyphemus*) were highly efficient for the removal of azinphosmethyl (Gulen et al., 2005). Liu et al. (2009) used raw- and acid-pretreated bivalve mollusk shells to remove metals from solutions and determined that the acid-pretreated shells were more efficient (Liu et al., 2009). However, all these processes produce secondary contamination.

In this study, the shells of the bivalve mollusk *Anadara inaequivalvis* were used as biosorbents for removing heavy metals from aqueous solutions, with no prior chemical pretreatments. *A. inaequivalvis*, has been introduced into Black Sea accidentally. They were transferred from Indo-Pasific region into Adriatic and Aegean and Black Sea throug ballast waters during 1970s. Although *A. inaequivalvis* have not consumed in Turkey, but there is high demand from European and the Far East markets (Sahin et al., 2009). This is the first study to utilize this type of seashell for heavy metal ion removal from aqueous solution. The objective of the present work is to characterize and investigate the biosorption potential of *A. inaequivalvis* shells in the removal of Pb(II) and Cu(II) ions (these common metals were easily found in environmental) from aqueous solution. The characterization of the biosorbent was done using the X-ray diffraction (XRD) and the Brunauer–Emmett–Teller (BET). Scanning electron microscope (SEM) and Fourier transforms infrared spectra (FT-IR) were also used before and after biosorption. Optimum biosorption conditions were determined as a function of pH, biosorbent dosage, contact time, heavy metal concentration, and temperature. The Langmuir, Freundlich, and Temkin models were used to describe the equilibrium isotherms. Biosorption mechanisms of Pb(II) and Cu(II) ions onto *A. inaequivalvis* shells were also evaluated in terms of thermodynamics and kinetics.

2. Materials and methods

2.1. *Chemicals and preparation of biosorbent*

A. inaequivalvis shells, which are widely available on the coast of the Black Sea, were collected from Beşikdüzü (Trabzon, Turkey). The shells were washed tap water, brushed to eliminate any attached contaminants, washed again with deionized water, and then dried at 100 °C for 24 h. The clean and dry seashells were crushed into smaller pieces, then ground and sieved to 250 μm. The biosorbent powder was stored in airtight acid washed Polyethylene containers at room conditions. Standard 1000 mg/L Pb (II) and Cu(II) ion solutions were prepared from their nitrate salts (Merck, Germany). For pH adjustment 0.1 M HCl and NaOH solutions were used. All the chemicals were analytical grade.

2.2. *Instrumentation*

An analytical grinding mill (Model A10, IKA, Germany) was used to grind the seashells. The seashell powder was sieved to 250 μm using a nylon sieve FT-IR of the raw and heavy metal loaded seashell powders were recorded using an ATR Bruker-Tensor 27 (Bruker, Bremen, Germany) spectrometer. The morphology and surface structure of the seashell powder, before and after heavy metal biosorption, were examined using a JEOL JSM 6060 (Jeol Ltd, Tokyo, Japan) SEM. The surface area (S_{BET}) was calculated using the BET equation with Micrometric, ASAP 2020 apparatus. The XRD crystallographic analysis was performed using a Rigaku Miniflex II diffractometer (Japan). The X-Ray analysis was done in the 2θ range from 10 to 80 (accumulation rate of 0.02 min^{-1}). A Perkin Elmer model Flame AAnalyst 800 Atomic Absorption Spectrometer (FAAS) was used for the quantitative analysis of Cu(II) and Pb(II) ions. pH measurements were performed using a Hanna pH 211 model pH-meter and many type of magnetic stirrers were used.

2.3. *Biosorption process*

For metal biosorption, batch adsorption experiments were performed by stirring (140–400 rpm) a known amount of seashell powder with 25.00 mL of the metal solution (Cu(II) or Pb(II)) in a 50.00 mL Erlenmeyer flask. The effect of the stirring rate was studied and a high biosorption capacity was obtained at 350 rpm; all other experiments were performed at this speed. The effect of other parameters on the biosorption capacity were investigated, including contact time (2.5–60 min), initial pH of metal (Cu(II) and Pb(II)) solutions (pH 2–6), amount of added biosorbent (1.5–10 mg), temperature (25–50 °C), and initial metal concentration (20–100 mg/L). From the results of the latter, the biosorption isotherms were developed. The amount of Ca(II) ions released from the biosorbent during the experiment was determined through EDTA