Copper(II) Adsorption by Biochar Fiber-MnO_2 Composites

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ABSTRACT

The adsorption efficiency of biochar fibers obtained from *Opuntia ficus Indica* cactus regarding the removal of Cu(II) ions from aqueous solutions has been investigated prior and after MnO_2 surface-deposition. The removal efficiency has been studied as a function of pH, Cu(II) concentration, ionic strength, temperature and contact time. In addition, the biochar fibers have been characterized by FTIR studies to elucidate the adsorption mechanism. Evaluation of the experimental data indicated that the MnO_2-composite product presents higher adsorption capacity, which is attributed to the formation of inner-sphere surface complexes, and that the adsorption reaction is a relatively fast and endothermic process. The results of the present study reveal that MnO_2-biochar composites could be used as very effective adsorbents for the removal of bivalent metal-ions from contaminated waters.

Key words: adsorption, biochar fibers, MnO_2-biochar composites, copper(II), waters

INTRODUCTION

Removal of toxic metal ions from large volumes of industrial process solutions and (waste)waters is of particular interest with respect to environmental protection and sustainable development. However, successful water treatment methods require a cost effective remediation technology. Conventional technologies relying on mineral adsorbents or chemical flocculating agents are relatively expensive and hence recently biosorption is presented as an alternative method for the removal of toxic metals from industrial process solutions and wastewaters [1]. Biosorption technologies based on living or dead biomass for accumulation and removal of heavy metals from aqueous solutions often replaces conventional processes in (waste)water treatment [1].

However, regarding living biomass (e.g. microbial systems) the major drawback is the price of growing a sufficient quantity of bacterial or algae biomass. Hence, the efforts have been focused on plant tissues and a variety of biomasses that represent by-products of various commercial activities (e.g. agriculture, food industry) have been investigated. The respective studies indicate that biomass by-products could represent good candidates for the development of inexpensive biosorption-based processes. Biomasses and particularly plant tissues are very abundant, non-hazardous materials, low cost, and can be easily disposed by incineration [1-5].

Adsorption of toxic metal ions on minerals [7, 8] and biomasses [1-5] is extensively investigated. Moreover, there are several studies dealing with metal adsorption on non-treated and chemically modified biomass by-products [1-5, 9-15]. Those modifications include surface oxidation, derivatisation as well as coating with metal oxides to enhance selectivity towards specific metal ions [5, 16]. There are also studies dealing with metal ion adsorption by carbon-based composite materials of interesting adsorbent properties such as selectivity, increased adsorption capacity, magnetism etc. [16, 17].

The present study deals with the adsorption of Cu(II) by biochar fibers derived from *Opuntia Ficus Indica* prior and after MnO_2 deposition. MnO_2 deposition on the biochar fibers is expected to enhance their separation efficiency and selectivity towards bivalent metal ions [6, 18] and Cu(II) has been used as analogue for bivalent toxic metal ions such as Cd(II) and Pb(II). The present study aims to investigate the effect of of various parameters (e.g. pH, copper concentration, ionic strength, temperature and contact time) on the biosorption performance and determine thermodynamic parameters (e.g. K_d, ΔG^o, ΔH^o and ΔS^o), which are of fundamental importance for both the assessment of the chemical behavior of bivalent metal ions in aquatic environments and the development of water treatment technologies. Moreover, FTIR studies have been performed to elucidate the mechanism upon adsorption is based.

MATERIALS AND METHODS

All experiments were performed at room temperature (23 ± 2 ^oC) under ambient conditions in aqueous solutions and constant ionic strength. Generally, the experiments were performed in duplicate and the mean values have been used for data evaluation. The preparation of the metal–ion solutions was carried out using a standard solution, and the Cu(II) concentration in solution was determined by potentiometry using a copper ion-selective electrode, which was calibrated before and after each experiment. pH measurements were performed by a commercial glass electrode, which was calibrated using a series of buffer solutions (pH 2, 4, 7 and 10). The adsorbents used in this study were biochar fibers prepared from *Opuntia ficus Indica* cactus fibres as described elsewhere [2, 4, 6].

Biochar fibers

Dried cactus cladodes were collected from local plants and the fibers of the cladodes were removed, washed thoroughly by distilled water and dehydrated at 110 ^oC for 15 h. Following the fibers were carbonized under N_2-atmosphere and oxidized (OCF) by means of 8 M HNO_3, as described elsewhere [9-15]. The product was sieved and the particle fraction between 200 and 500 μm was selected for the adsorption experiments. The preparation of the MnO_2-biochar fiber composites was carried out using $KMnO_4$ solutions as described elsewhere [2, 4, 6, 19]. The determination of the morphology of the fibers was carried out by scanning electron microscopy (SEM, Vega TS5136LS- Tescan), specific surface area measurements were based on the Brunauer–Emmett–Teller theory (BET measurements) by means of N_2-adsorption (ASAP 2000, micromeritics) and FTIR spectroscopic measurements (FTIR spectrometer 8900, Shimadzu) were performed by means of prepared translucent KBr disks including finely ground biochar fibers encapsulated at a 10:1 mass ratio, prior and after Cu(II) adsorption.

Adsorption measurements

In order to investigate the effect of various parameters (pH, copper concentration, ionic strength, temperature and contact time) on the Cu(II) adsorption on oxidized biochar fibers (OCF) and MnO_2-biochar fiber composites (OCF-MnO_2), different classes of experiments were conducted. In these experiments the parameter under investigation was varied, while other experimental parameters were kept constant. All test solutions were prepared using 0.1 M $NaClO_4$ (Aldrich Co.) as the background electrolyte. The effect of pH was studied in an adsorption system (0.01 g adsorbent and 20 ml of the test solution [Cu(II)]= 5×10^{-4} M) in which pH was varied between 2 and 9 by addition of $HClO_4$ or NaOH. The other parameters were studied at pH 3 and pH 5 for OCF and OCF-MnO_2, respectively, which were the self-adjusted pH values for the two systems. The effect of the ionic strength (salinity) was studied by addition of $NaClO_4$ salt to prepare solutions of various concentrations (0.001, 0.01, 0.1, 0.5, 0.7 and 1 M) at constant adsorbent amount (0.01 g), total copper concentration (5×10^{-4} M). For studying the effect of initial copper concentration, the latter was varied between 5×10^{-6} M and 9×10^{-3} M, at a prefixed amount of adsorbent (adsorbent dosage= 0.01 g and the optimum pH value for each adsorbent). The effect of temperature was studied between 30 and 70 ^{o}C at the same conditions that are described above. For kinetic studies a certain amount of the biomasses (0.01 g) was mixed with 20 ml of copper solution (5×10^{-4} M). After an equilibration time of 24 hours the metal concentration was determined by potentiometry using a copper ion selective electrode. For each test solution, a corresponding reference solution was prepared and was similar to the test solution except that it didn't contain the adsorbent material. Experiments and data evaluation has been performed as described elsewhere [6, 8, 14, 15].

RESULTS AND DISCUSSION

Fiber Characterization

In order to prove the formation of the biochar fiber MnO_2-composites (OCF-MnO_2), the products were examined by X-ray powder diffraction (XRD) and a representative XRD diffractogram is shown in Figure 1. The diffraction peaks at 2θ= 25.4, 36.5, 41.5 and 65.9 from the biochar fiber MnO_2–composites match the standard XRD pattern of the manganese oxide (JCPDS 80-1098), indicating the successful deposition of MnO_2 on the biochar surface [6, 20]. The broad peak at 2θ= 24^{o} is characteristic for graphite-type materials [9, 13].

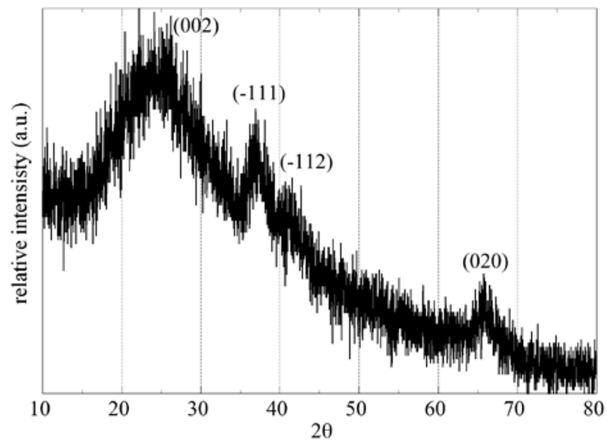

Fig. 1 XRD difractograms of *Opuntia figus Indica* biochar fibres after MnO_2 deposition

In addition, Figure 2 presents a SEM image of biochars fibers after MnO_2 deposition, which clearly shows distinct MnO_2 crystallites formed on the biochar surface (white spots) and that chemical modification did not affect the texture of the fibers. Even after chemical modification the fibers keep their laminated texture, which is responsible for their increased external surface. However, BET measurements indicate that there is no internal mesoporous surface (BET surface <5 m^2 g^{-1}), which is expected for plant fibers carbonized at temperatures below 650 ^oC.

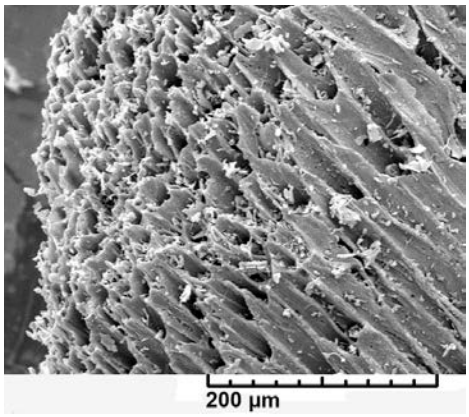

Fig. 2 SEM image of *Opuntia figus Indica* biochar fibres after MnO_2 deposition

pH effect

The relative adsorption is related to the chemical affinity of the surface for the adsorbate, which depends on both the chemical behavior of Cu(II) ions in solution and the surface charge of the adsorbent. Hence, the solution pH is an important parameter affecting adsorption on surfaces, because pH may govern both the chemical behavior of a metal ion in solution and the surface charge of an adsorbent. To study the effect of pH on the Cu(II) adsorption, samples of the two different biochar products were conducted with Cu(II) solutions at different pH values (2 < pH < 9).

The effect of pH on the relative adsorption of Cu(II) by the two different biochar materials (OCF and OCF-MnO_2) is shown in Figure 3. In the case of the non-treated cactus fibers the relative adsorption increases with increasing pH and reaches a maximum value (~100%) for pH > 5. For pH values below 5 the relative adsorption decreases with pH due to the protonation of the surface carboxylic and/or hydroxy groups which are present at the surface of the oxidized biochar fibers and their MnO_2 composites, respectively, and bind the Cu(II) ions as described schematically for instance by Equations 1 and 2.

$$=S\text{-}COOH + Cu^{2+} \leftrightarrow =S\text{-}COO\text{-}Cu^{+} + H^{+} \quad (1)$$

$$=S\text{-}OH + Cu^{2+} \leftrightarrow =S\text{-}O\text{-}Cu^{+} + H^{+} \quad (2)$$

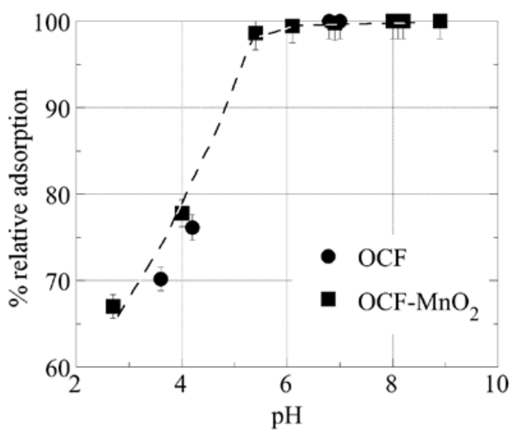

Fig. 3 The effect of pH on the relative adsorption of Cu(II) by biochar fibers prior and after MnO_2 surface deposition

Effect of Cu(II) concentration

In order to evaluate the maximum adsorption capacity (q_{max}) adsorption experiments with varying copper concentrations have been performed at the optimum pH for each adsorbent. The corresponding isotherms, which have been well fitted Langmuir isotherm model, are graphically shown in Figure 4 and indicate that the biochar fiber MnO_2-composites (q_{max}= 5.0 ±0.2, R^2= 0.98) present higher adsorption capacity for

Cu(II) than the non-modified biochar fibers (q_{max}= 2.1 ±0.1, R^2= 0.99). The q_{max} value of the composite material shows that chemical modification of the material improves its adsorption attributes, and that biochar fiber MnO_2–composites can be used as an alternative for MnO_2 resins [19].

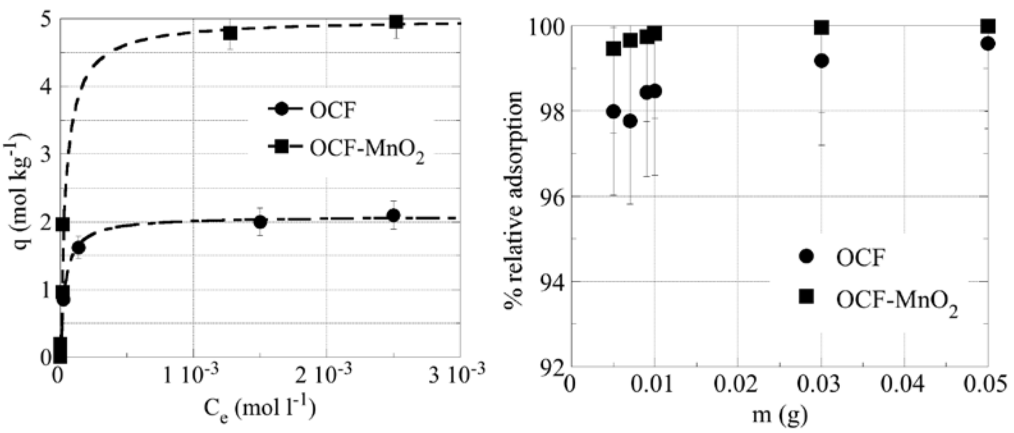

Fig. 4 Adsorption isotherms and the effect of the adsorbent mass on the relative adsorption corresponding to Cu(II) adsorption by biochar fibers prior and after MnO_2 surface deposition

The effect of ionic strength/salinity on the adsorption efficiency

Furthermore, the effect of ionic strength 0.001, 0.01, 0.1, 0.5, 0.7 and 1 M [$NaClO_4$) on the relative adsorption of Cu(II) was investigated, in order to understand the interaction mechanisms on which Cu(II) binding on the two different types of biochar materials is based. The experimental data obtained from the corresponding experiments are graphically summarized in Figure 5 and show clearly that the relative adsorption of the oxidized (OCF) and the biochar fiber MnO_2-composites (OCF-MnO_2) is not affected by increasing salinity indicating specific interactions between Cu(II) and the active surface groups (carboxylic and hydroxy groups) of the respective adsorbents. Hence, the adsorption can be attributed to the formation of inner-sphere complexes, which are only little affected by salinity changes [6, 21].

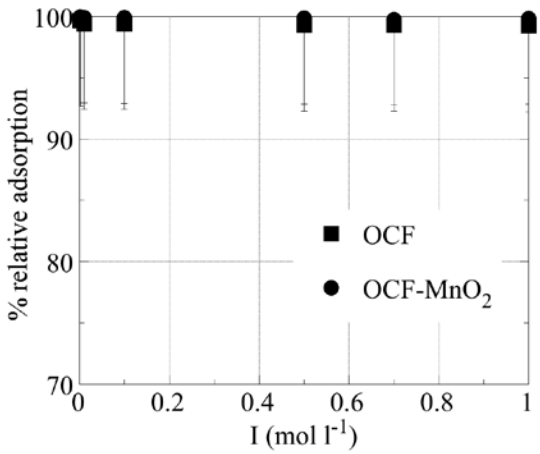

Fig. 5 The effect of ionic strength on the relative adsorption of Cu(II) by biochar fibers prior and after MnO_2 surface deposition

Moreover, *Fourier* transform infrared (FTIR) spectra were recorded to identify the functional groups and elucidate the adsorption mechanism corresponding to the Cu(II) adsorption by the biochar adsorbents prior and after modification. The FTIR spectra of oxidized biochar fibers (OCF) and the corresponding MnO_2-composites (OCF-MnO_2) before and after Cu(II) adsorption are shown in Figure 6. The IR spectra of the oxidized biochar fibers (OCF) show main absorption bands at 3433, 1717, 1610, 1342 and 1250 cm^{-1}. The broad band around 3433 cm^{-1} corresponds and the others bands to stretching and bending modes of the carboxylic moieties present at the biochar surface. After Cu(II) adsorption and depending on the Cu(II) concentration the relative intensity of the bands attributed to the carboxylic moieties changes dramatically indicating the formation of inner-sphere complexes between Cu(II) and the surface active species [14] and are in agreement with the results obtained from the experiments related to the effect of salinity.

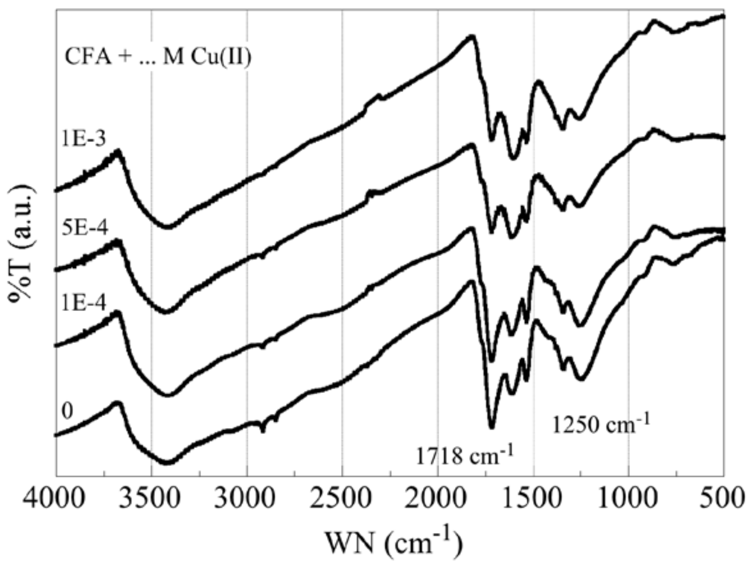

Fig. 6 FTIR spectra of the oxidized biochar fibers (OCF) prior and after successive Cu(II) adsorption

Regarding the FTIR spectra of the biochar MnO_2-composites (Figure 7), the broad bands at ~3369 cm^{-1} are attributed to –OH groups, and the peaks at 2927 and 2856 cm^{-1} correspond to CH_2 deformation vibrations. The bands in the region between 1730 and 1450 cm^{-1} are ascribed to aliphatic or aromatic groups (e.g. C=C), and carbonyl C=O stretching vibrations. The peak at 1360 cm^{-1} is associated with –OH vibrations and the broad band observed after MnO_2 deposition in the low-frequency region around 510 cm^{-1} corresponds to Mn–O vibrations. After Cu(II) adsorption, the relative intensity of the characteristic bands at 1580, 1360 and 511 cm^{-1} changes significantly indicating that mainly the hydroxyl groups of the MnO_2 phase bind the Cu(II) ions to form stable inner-sphere complexes (e.g. Mn–O–Cu) [22] and are in agreement with the results obtained from the experiments related to the effect of salinity. The broad peak at 510 is a characteristic absorption band of birnessite, corresponding to Mn-O stretching modes of the octahedral layers in the birnessite structure which is consistent with the previous XRD result.

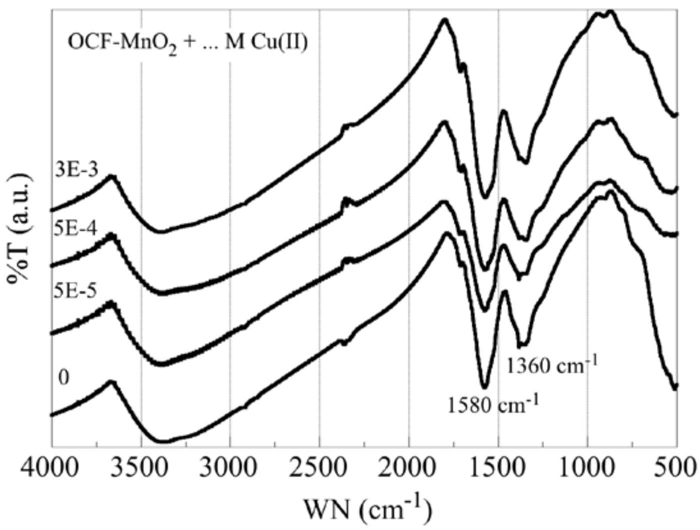

Fig. 7 FTIR spectra of the oxidized biochar fiber MnO_2-composites (OCF-MnO_2) prior and after successive Cu(II) adsorption

The effect of temperature on the adsorption efficiency

The effect of temperature on Cu(II) adsorption biochar fibers prior and after MnO_2 surface deposition was investigated to estimate the corresponding thermodynamic data based on the van’t Hoff equation. Evaluation of the data (Figure 8) shows that adsorption of Cu(II) on the biochar composites (OCF- MnO_2) is an endothermic and entropy-driven spontaneous process (ΔH^o = 15.6 kJ mol^{-1}, ΔS^o = 156.7 J mol^{-1} K^{-1}, R=0.90). On the other hand, adsorption of Cu(II) on the oxidized biochar fibers (OCF) is an exothermic process (ΔH^o = -22.3 kJ mol^{-1}, ΔS^o = 2.0 J mol^{-1} K^{-1}, R=0.95). Generally, the values of the thermodynamic parameters evaluted are close to corresponding values reported in the literature for similar systems [6, 23, 24].

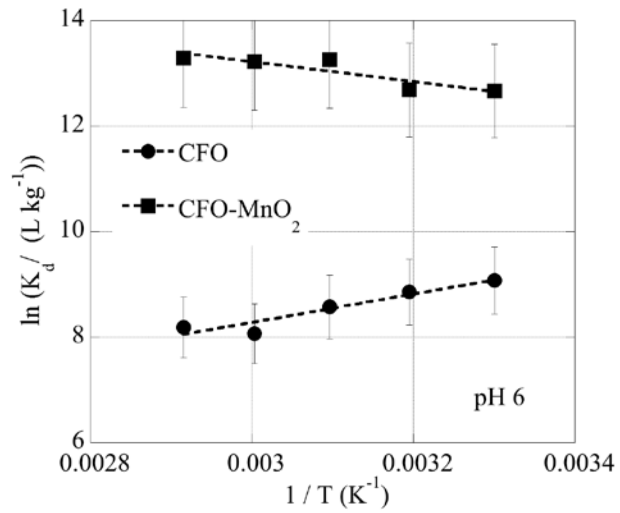

Fig. 8 The effect of temperature on the relative adsorption of Cu(II) by biochar fibers prior and after MnO_2 surface deposition

Kinetic measurements

According to Figure 9, which shows the relative amount of adsorbed Cu(II) as a function of time, the adsorption of Cu(II) by the two different biochar materials is a two step process with a relatively first fast step which could not be followed by the potentiometric method and a second slow process related to the diffusion of the Cu(II) ions within the fiber channels/tubules.

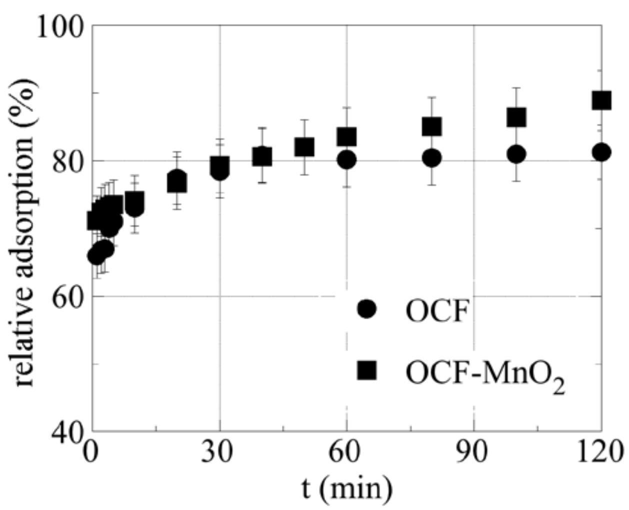

Fig. 9 Time-depended relative adsorption of Cu(II) by biochar fibers prior and after MnO_2 surface deposition

CONCLUSIONS

In this study oxidized and MnO_2-modified biochar fibers prepared from O. ficus-indica cactus fibres were used to adsorb Cu(II) ions from aqueous solutions. SEM and XRD measurements indicate the successful preparation of the OCF-MnO_2 composites and the experimental data indicate increased affinity of both materials for Cu(II), which is further improved by chemical modification and the formation of MnO_2-composites. The equilibrium data were described well by a Langmuir isotherm, indicating that the adsorption of copper on biomass is based on specific chemical interactions, which is corroborated by experiments of varying ionic strength/salinity and FTIR studies prior and after Cu(II) adsorption. The thermodynamics change dramatically upon MnO_2 deposition indicating different adsorption mechanism and adsorption kinetics are relatively fast for both materials.

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