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Sorption of copper and zinc using fibres of *Cocos nucifera*

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ABSTRACT

*Fibres of *Cocos nucifera* (coir) is a low cost biosorbent that has been used for the removal of zinc and copper metal ions from aqueous solutions. Batch sorption experiments were carried out with Zn (II) and Cu (II) to quantify the sorption kinetics, the pH dependence of the sorption, sorption isotherms at pH 3.0 and pH 5.6, and desorption. Ungrounded and unmodified coir was used and the metal concentrations ranged between 0 and 0.015 mM (1000 μgL^{-1}) for Zn (II) and 0 and 9.7 10^{-4} mM (200 μgL^{-1}) for Cu (II). The optimum pH was 4.5 (91%) for zinc and 3.5 (97%) for Copper removal. Copper had a higher sorption affinity than Zinc and the affinity was higher at pH 5.6 than at pH 3.0. The sorption data fitted well the Freundlich model in the concentration range tested. Desorption experiments demonstrated that less than 1% and 13% of the sorbed Copper and Zinc, respectively, could be desorbed at pH 5.6 during 2 h.*

Keywords: Biosorption; Copper; Zinc; Isotherms; Desorption.

INTRODUCTION

A delicate balance exists between man and the environment. Lately, this balance has been seriously disturbed by man's direct as well as indirect activities. The presence of metals like Cd, Hg, Pb, Cr, Ni, Cu, Zn, and Co is, at elevated concentrations, detrimental to human health and ecosystem stability. In order to reduce pollution, biosorption is an alternative to conventional methods such as chemical precipitation, ion exchange, electrolysis, membrane filtration for removal of heavy metals from industrial wastewater because these processes have the limitations of technical and/or economical viability [1-5]. Biosorption is not restricted to one sorption mechanism only, but comprises several mechanisms such as ion exchange, chelation, precipitation, sorption by physical forces, and ion entrapment in inter- and intrafibrillar capillaries and spaces of the structural lignin and polysaccharide networks [6-7]. The literature

survey reveals two distinct approaches to the use of biosorbents, either of living microorganisms or non-viable (dead) biomass of microorganism and agricultural waste [8-11]. Plant fibres consist mainly of lignin, cellulose, hemicellulose, and some pectin and extractives (mainly fat, fatty acids, fatty alcohols, phenols, terpenes, steroids, resin acids, rosin and waxes). Metal ions adsorb mainly to carboxylic (primarily present in pectin and hemicellulose but also extractives and lignin), phenolic (lignin and extractives) and to some extent hydroxylic (cellulose, hemicellulose, lignin, extractives, and pectin) and carbonyl groups (lignin) [12-14]. Strong bonding of metal ions by the hydroxylic, carboxylic and phenolic groups often involves complexation and ion exchange [6-7]. Thus, for metal removal applications, the use of dead biomass or agricultural waste may be preferable as large quantities are readily and cheaply available as a byproduct of various industries [15-20]. Coir (fibres from *Cocos nucifera*) is a waste product from the copra industry. The fibre consists of one or more vascular bundles surrounded by heavy fibre sheaths. The fibres are surrounded by lignified ground tissue (stone cells). The objectives of the present investigation were to study the sorption of Zn and Cu to unmodified and unground coir at relative low concentrations with particular focus on sorption kinetics, the pH dependence of sorption, sorption strength and capacity, and reversibility of the sorption process. Cu and Zn were chosen because they represent two rather different types of metal ions with different binding affinities and mechanisms, Cu usually forming stronger complexes (like e.g. Co, Ni, and Pb) than Zn (and e.g. Cd and Mg).

EXPERIMENTAL SECTION

2.1 Physico– Chemical Analysis of the biosorbent

The coir was bought from M/s Shubham Copra Industries, Puri, Orissa. It had been industrially defibrated after a retting process. Portions of plant fibres were taken evenly spaced in the batch. The fibres were cut into parts of 2–3 cm and mixed. It was used in experiments with washing thrice with double distilled water to remove soluble lighter materials and drying at 120⁰C in an oven. The content of major components of the coir cell wall was determined by a gravimetric method with sequential removal of water soluble extractives (extracted with hot water), pectic substances (extracted with EDTA), lignin (extracted with NaClO₂ and HCl) and hemicellulose (extracted with NaOH and H₃BO₃), leaving the cellulose component in the sample [21]. The content of metal ions found in fibres of *Cocos nucifera* is given in Table 1.

2.2. Sorption

2.2.1. Pre-treatment of the fibre

Due to the large affinity of Cu to sorb to glass as well as to polyethylene (PE), it was necessary to use Teflon tubes for the Cu sorption experiments. As Zn's affinity to PE was not a problem, PE vials were used for the Zn experiments. Preliminary tests showed that sorption of Zn and Cu ions to these respective container materials were negligible. The methods were developed working with Zn sorption and then adapted to Cu sorption. The methods varied a little between the two metals. In general, experiments were carried out in the following way. Before sorption, the fibres were swelled in electrolyte (0.01 M NaNO₃) for 3 days on a shaking table (110 rpm). In the case of Zn, 1.00–1.01 g of fibre was swelled in 100 ml polyethylene (PE) vials with 50 ml electrolyte, and in the case of Cu, 0.33–0.34 g of fibre was swelled in 17 ml Teflon centrifuge tubes with 15 ml electrolyte. For observations at pH 3.0 and the pH dependency experiments, the pH was adjusted with dilute HNO₃ or NaOH, to the pH wanted for the sorption, before swelling. After the sorption, in the case of Zn, 25 ml supernatant were transferred to a PE centrifuge tube and centrifuged at 12,000 rpm for 20 min and thereafter 15 ml supernatant were preserved for analysis. In the Cu experiments, the fibres and electrolyte with metal ions were centrifuged in the same tube they were swelled in, and thereafter 10 ml supernatant were preserved. All samples

were preserved in PE vials by acidification with HNO₃ (final concentration 0.1 M) and stored in a refrigerator. At 0.1 M H⁺, there was no problem with sorption of Cu ions to the PE vials. When relevant, the following three controls were included: (1) electrolyte without fibres, but with metal ions added, (2) electrolyte with fibre, but without metal ions added, and (3) electrolyte with neither metal nor fibre added.

2.2.2. Effect of initial metal concentration and contact time

Initially, experiments were carried out to determine the time needed to reach equilibrium. These experiments were carried out at pH 5.6 and initial concentrations of 0.0015 mM Zn, 0.0031 mM Zn, and 9.7 x 10⁻⁴ mM Cu. Samples were withdrawn after 10 min, 30 min, 1 h, 2 h, 4 h, 6 h, 10h. The experiments ran in duplicate or triplicate.

2.2.3. Effect of pH

The variation of sorption with pH was determined by measuring the relative amounts of Zn and Cu adsorbed at different pH values ranging between pH 1 and 7 (Zn) and 1 and 5.7 (Cu) at fixed starting metal ion concentrations of 0.0031 mM Zn and 9.7 x 10⁻⁴ mM Cu, respectively. The pH was adjusted before swelling and was readjusted immediately after adding metal solutions. After sorption, pH and the metal concentration in solution were measured.

2.2.4. Sorption isotherms

Sorption isotherms were determined at pH 3.0 and 5.6 with the following initial concentrations: 0–0.61 mM Zn (at pH 5.6), 0–0.015 mM Zn (at pH 3.0), 0–0.097 mM Cu (at pH 5.6) and 0–0.0014 mM Cu (at pH 3.0). The fibre swelled in electrolyte with pH adjusted to 3.0 and 5.6, respectively. Immediately after adding metal solution, the pH was readjusted. Because the sorption is rather sensitive to pH around pH 3.0, the sorption at this pH was calculated using the regression and interpolation technique described by Tiller *et al.* [22] in which three samples were carried out for each initial metal ion concentration—one with pH slightly below 3.0 (2.6–2.9), one with pH as close as possible to pH 3.0 (2.8–3.2) and one with pH slightly above pH 3.0 (3.2–3.5). There were no further replications. The sensitivity of sorption to pH variations around pH 5.6 was not critical (Table 2), and sorption experiments at that pH were carried out with normal duplicate or triplicate replications and without use of the regression technique. In the experiment at pH 5.6, the pH was between 5.3 and 5.9 after sorption. The sorption isotherms were tested for fit to the Langmuir (1916) and Freundlich (1906) models:

$$\text{Langmuir: } S = \frac{S_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (1)$$

$$\text{Freundlich: } S = K_F \cdot C_e^{1/n} \quad (2)$$

where S is the amount of metal sorbed by the fibre (mg/g or mmol/g fibre), S_{max} is the maximum amount of metal which may be sorbed by the fibre (mg/g or mmol/g fibre), C_e is the metal concentration in the solution at equilibrium (mg/l or mM), and K_L (l/mg or l/mmol), K_F (mg^(1-1/n) l^(1/n)/g or mmol/g mM^(1/n)), and n (dimensionless) are constants. The constants, including S_{max}, are specific for the sorption and dependent on temperature and pH among others. The values in the models were found with an iterative nonlinear regression model using the statistical program SAS [23].

2.2.5. Desorption

In order to test the reversibility of the sorption process, desorption experiments were carried out using fibres which had adsorbed Zn and Cu at pH 5.6 at initial solution concentrations of 0.0031

mM Zn, 0.012 mM Zn, 9.7×10^{-4} mM Cu, and 0.0019 mM Cu. Desorption times ranged between 10 min and 7 days. In the case of Zn, the fibres were picked up from the sorption solution and centrifuged (12,000 rpm for 20 min) to remove excess liquid, followed by transfer of the fibres to a new PE flask with fresh electrolyte. After different desorption times the supernatant was transferred to a centrifuge tube and preserved as in the sorption experiments. In the experiments with Cu, the supernatant was removed after sorption and the fibres were centrifuged in the same Teflon tube in which swelling took place. The free liquid was sucked up, and fresh electrolyte was added. After desorption, the tube was centrifuged and 10 ml supernatant were preserved as in the sorption experiments. All experiments ran in duplicate. The pH after desorption was 5.0–5.8.

2.2.6 Chemicals and equipment

All chemicals were analytical grade and purchased from E Merck, India Ltd., Mumbai, India. Zn and Cu stock solutions (1000 mg/l) for use as standards and in sorption experiments were prepared from $\text{Cu}(\text{NO}_3)_2$ and ZnCl_2 , respectively. Double distilled water was used throughout. Zn was measured by atomic absorption spectroscopy (Perkin–Elmer 3300) and Cu by graphite furnace atomic absorption spectroscopy (GFAAS; Perkin–Elmer 5100 with Zeeman correction). The temperature was between 20 and 25 °C during all experimental work.

RESULTS AND DISCUSSION

3.1. Effect of initial metal concentration and contact time

The extent of sorption increased rapidly in the initial stages but became slow in the later stages till the attainment of equilibrium. More than 80% of the metal ions were sorbed within the first 40 min (Fig. 1). The kinetic data did not fit with the parabolic diffusion law and hence intra particle diffusion is not the only factor that controlling the rate of Zn and Cu sorption to coir, indicating that chemical bonding also affects the rate of sorption. However, depending on the structure and composition of the fibres, the access to reactive sites may be more or less hindered, and thus sorption may become controlled by diffusion rates after an initial period of fast sorption [7]. The generally fast reactions indicate that reactions at outer surfaces are important.

3.3. Effect of pH

The sorption of Zn was sensitive to pH up to the maximum sorption at pH 4.5 and sorption of Cu increased from zero to maximum within the pH range 1–3.5 (Fig. 2). At pH below 2.7, Zn was released from the coir amounting to a maximum of 7.3×10^{-5} mmol/g fibre (4.8 µg/g), which is in reasonable agreement with the measured native Zn content in the coir (4.32 µg/g or 6.61×10^{-5} mmol/g) (Table 2). At maximum, the sorption was 91–93% (Zn) and 95–97% (Cu) of the initial metal loaded. The observations for Zn are in reasonable agreement with the literature [21]. In case of Cu, most studies have shown that Cu sorption increases up to a higher pH level than that found in the present study [12, 25-26].

3.4. Sorption isotherms

The affinity for sorption was considerably higher for Cu than for Zn, and higher at pH 5.6 than at pH 3.5 for both metals (Fig. 3a and 3b). At pH 3.5, some Zn was released below a concentration of about 0.0028 mM. Due to this considerable release of Zn, a modified isotherm for Zn at pH 3.5 was constructed by calculating the sorption as the total amount of Zn (supply plus the natural content) minus what was left back in the solution after the sorption. This new isotherm describes the total ability to sorb Zn at pH 3.5. It is used in Fig. 3a and is referred to as ‘‘Zn isotherm at pH 3.5’’ in the following. The isotherms were tested for fit to the Langmuir model, but the model was not suitable for describing the sorption of either Zn or Cu at the pH and metal concentrations

tested. All isotherms could be represented by the Freundlich model within the 95% confidence interval for the model. All, except the Cu isotherm at pH 3.5, had a P-value in the F-test of the fit to the model at <0.0001 , while the Cu isotherm at pH 3.5 had 0.0031. All the R^2 -values for the Freundlich fits exceeded 0.993. The resulting estimates and the statistical parameters for the Freundlich model are listed in Table 2. K_F reflects the sorption affinity and $1/n$ expresses the curvature of the isotherm. As can be seen from the table, K_F is considerably higher for Cu than for Zn and for pH 5.6 than for pH 3.5. The difference between the two values for Zn is relatively higher than that between the two values for Cu, which can be partly explained by the fact that the pH optimum for Zn is not reached at pH 3.5 while the optimum for Cu is below pH 3.5 (Fig. 2), and therefore the change in sorption affinity with pH is less pronounced for Cu than for Zn. Except for the Zn isotherm at pH 5.6, the n constants of the Freundlich equation were close to 1, which means that the isotherms were close to being linear. The Zn isotherm at pH 5.6 not being linear can partly be explained by the fact that the isotherm was made at higher equilibrium concentration than the other isotherms, resulting in a more “Freundlich”-like curve. At pH 5.6, the sorption of Zn was actually higher than the sorption of Cu at very low concentration (below 2.3×10^{-4} mM), but because of the low value of $1/n$ for Zn, the Cu sorption exceeded Zn sorption at higher solution concentrations. Because of the knowledge about the heterogeneous structure of the fibres and the Langmuir model not fitting, it is attempting to assume that there was more than one mechanism dominating the sorption [27].

3.5. Desorption Studies

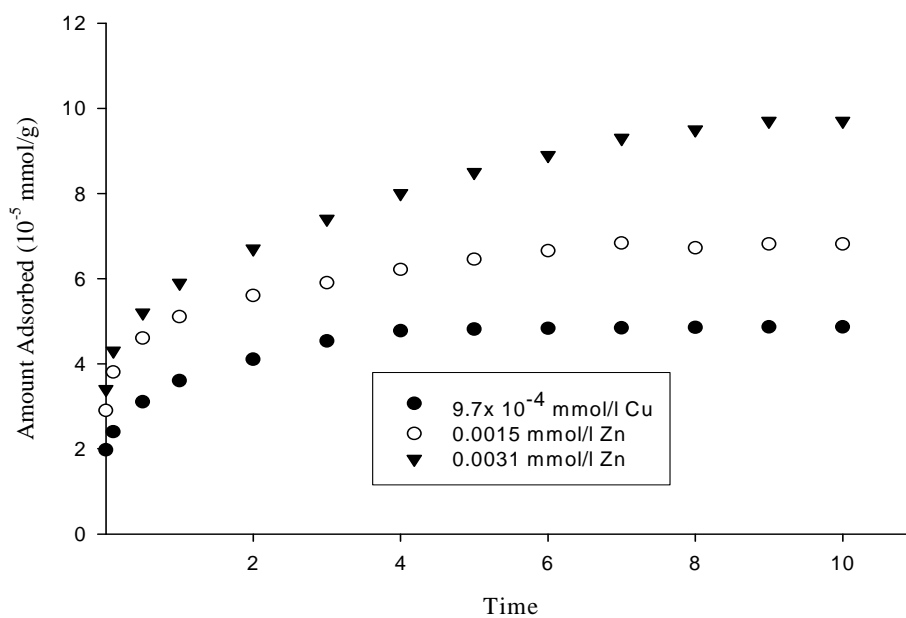
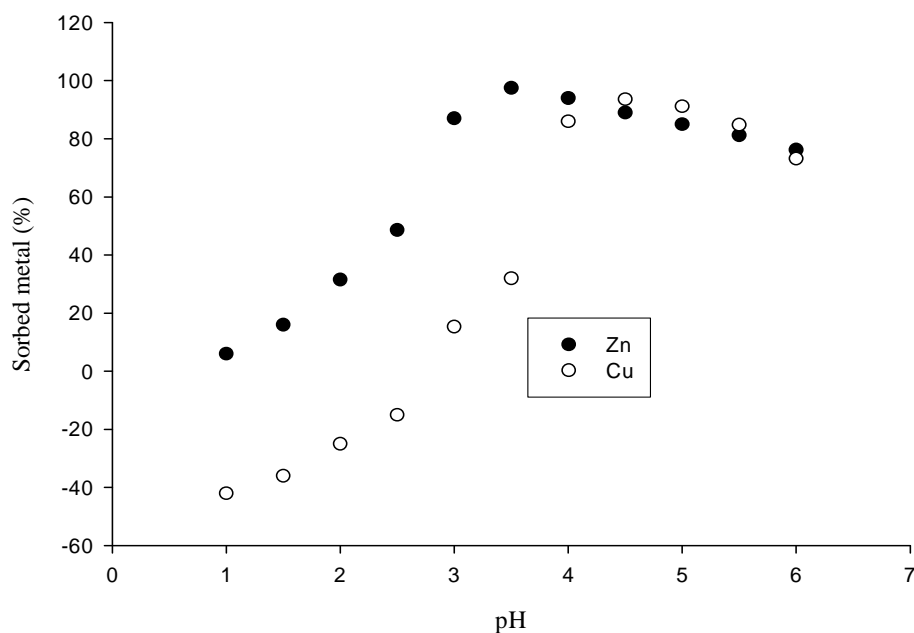
The main part of Zn and Cu desorption at pH 5.6 occurred within the first 10 min. As was expected from the knowledge of Cu forming stronger complexes than Zn, Zn desorbed to a higher degree than Cu. At equilibrium concentrations of Zn at 9.1×10^{-5} mM and 1.7×10^{-4} mM, 4.4×10^{-6} mmol/g fibre and 7.3×10^{-6} mmol/g fibre, respectively, were desorbed. At a solution Cu concentration below the detection limit, less than 3.4×10^{-7} mmol/g fibre was desorbed. On a relative scale more metal was desorbed at lower than at higher initial loadings. In the case of Zn, less than 13% was desorbed at the low initial concentration and 4% at the high. In the case of Cu, the release was less than 1% at the low as well as the high loading. This low desorption only counts at relatively high pH, as it is well known that it is possible to recycle the sorbent or the metal by cleaning the sorbent with acid [28-29]. The low desorption supported the assumption that covalent bonding is part of the metal sorption mechanism.

Table 1 Native content of metal in the fibres of *Cocos nucifera*.

Metal	$\mu\text{g metal/g fibre}$
Na	861
Mg	474
Al	52.5
P	79.8
K	3630
Ca	564
Mn	5.94
Fe	121
Co	0.054
Ni	0.715
Cu	3.12
Zn	4.32
Mo	0.035
Cd	0.020
Cu	0.175

Table 2 Values of Freundlich constants for Zn and Copper

Metal	pH	R ²	P ^a	K _F ^b	1/n
Zn	3.5	0.998	<0.0001	0.021	0.98
	5.6	0.993	<0.0001	0.384	0.75
Cu	3.5	0.997	0.0031	1.020	0.96
	5.6	0.994	<0.0001	2.460	0.97

**Fig. 1** Time variation plot for the adsorption of Cu and Zn**Fig. 2** Effect of pH on the removal of Cu and Zn by sorption on coir

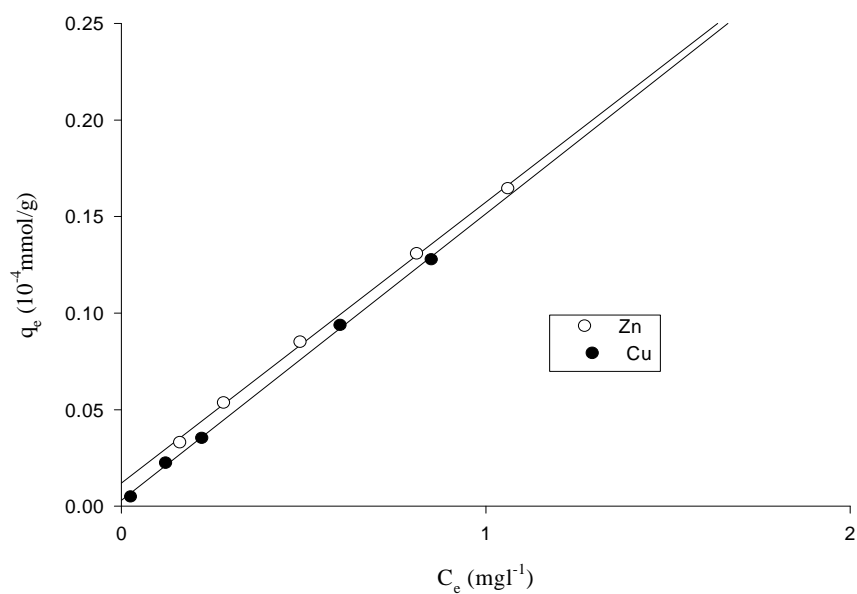


Fig. 3a Sorption isotherm plot for adsorption of Cu and Zn on coir at pH 3.5

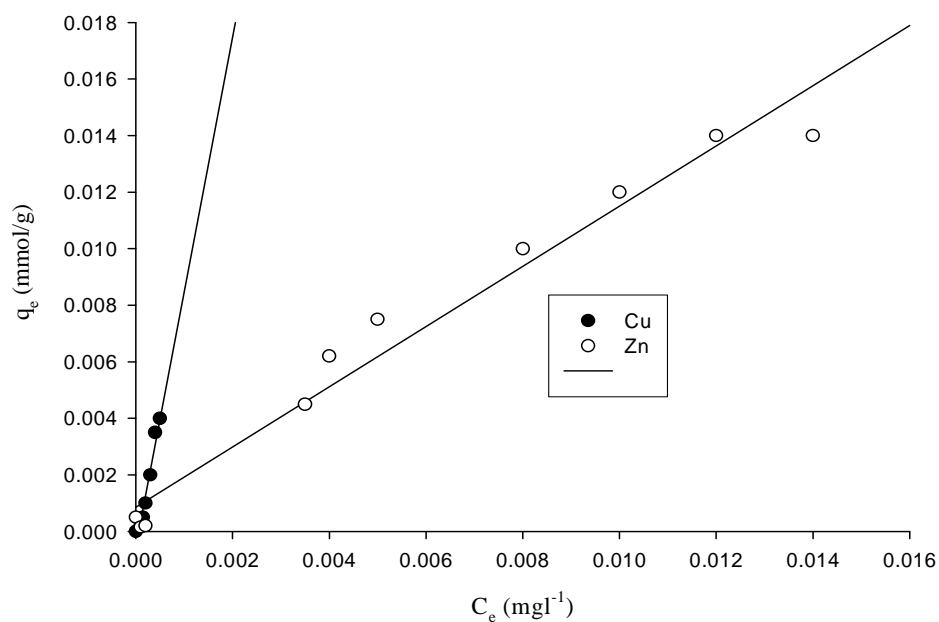


Fig. 3b Sorption isotherm plot for adsorption of Cu and Zn on coir at pH 5.6

CONCLUSION

Fibre of *Cocos nucifera* (coir) has a promising potential for being a metal ion sorbent. In the range tested, more than 80% of the metal was sorbed within the first 40 min and the total amount of metal sorbed was 91–97% of the metal initially added. Cu had a higher sorption affinity than

Zn. In addition to high affinity and capacity, the two most interesting properties of the coir biosorption are the low pH optima for sorption (pH 4.5 for Zn and 3.5 for Cu) and the low desorption (less than 13% for Zn and 1% for Cu), the low pH optima making it possible to use coir directly in cleaning acidic waste water without a prior pH increase. The sorption isotherms can be represented by the Freundlich equation within the concentration range tested. The low degree of desorption ensures that the metal ions will not desorb in situations with lowering of the metal concentration in the solution, e.g. caused by a periodic drop in the metal concentration level of the waste water. Those properties specific for coir are in addition to the properties always counting for using plant fibres as sorbents: being easily accessible, cheap, CO₂ neutral, and biodegradable. And in the form of a nonwoven mat, the sorbents are easily handled. Before applying coir for water cleaning purposes, further investigations are needed, the most important being sorption studied in flow experiments, desorption at low pH and competition between ions.

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