Removal of TDS from Cooling Tower Water by Using EDTA-Modified Bagasse Fibers

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Abstract: Modified by ethylenediaminetetraacetic acid (EDTA) salts and unmodified bagasse fibers were tested for the removal of total dissolved solids (TDSs) from cooling tower water. Parameters such as hydrogen ion concentration (pH), particle size of bagasse fibers, and the concentrations of adsorbent and adsorbate were studied to optimize the conditions to be applied on a commercial scale for the decontamination of effluents of cooling tower water. The optimum pH for TDS removal was between 6 and 6.5. The efficiency of TDS removal increased when the size of fiber particles decreased (100 μm) and when the concentration of EDTA salt increased to reach 78 mg/g of modified bagasse fibers. The adsorption parameters were determined using both Langmuir and Freundlich isotherms. The preferential mechanisms for the retention of TDSs are a complexation process between the TDSs and chemical functions present on the surface of fibers, and the chelation process with the EDTA attached to the fibers. The results obtained could be valuable for application to cooling tower water treatment and for the softening of hard drinking water.

CE Database subject headings: Salt; Fibers; Cooling towers; Cooling water; Water treatment.

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Introduction

Cooling towers can be a critical process in many industrial production facilities. As water evaporates, minerals and contaminants in the water concentrate. These minerals and contaminants will eventually reach a concentration where they will cause problems and interfere with the performance of both the tower and the cooling system itself. The fouling and corrosion of the cooling tower can impact treatment and heat transfer losses causing a decrease in efficiency and an increased power consumption. Corrosion can occur on the metal parts.

Scale forms by the precipitation of solids inside cooling system surfaces. Through the coating of primary heat exchange surfaces, these solids insulate the hot side from the cold side of the heat exchanger. A secondary effect is the blockage of water flow at the heat exchange tubes, cooling tower basins, or cooling tower fill.

Cooling loop scales are generally calcium carbonate crystals. In a few cases they are calcium sulfate or silica solids. Scaling occurs because specific dissolved solids have exceeded their solubility limits and form solids. The water contains more of a particular species than can be dissolved. For example, calcium carbonate crystals precipitate because the calcium and alkalinity levels exceed "saturation" at the water's pH condition.

Particulate contaminants collect over a period of time in the basin at the bottom of the tower and from time to time the tower must be shut down to clean out the contaminants which have settled therein. Such a cleaning procedure is costly in terms of downtime for the cooling system and the facility cooled by the cooling tower.

Laszlo and Dintzis showed that lignocellulosics have an ion-exchange capacity and general sorptive characteristics, which are derived from their constituent polymers and structure. The polymers include extractives, cellulose, hemicelluloses, pectin, lignin, and protein. These are adsorbents for a wide range of solutes particularly divalent metal cations (Laszlo and Dintzis 1994). Lignocellulosic resources all contain, as a common property, polyphenolic compounds, such as tannin and lignin, which are believed to be the active sites for attachment of heavy metal cations (Waiss et al. 1973; Masri et al. 1974; Randall et al. 1974; Bhattacharyya and Venkobacharc 1984; Phalman and Khalafalla 1988).

The biosorption of metals with selected inactivated microorganisms had been suggested as an alternative method to the existing metal recovering processes (Han et al. 1999; Aderhold et al. 1996; Simkovc et al. 1996; Morita et al. 1987). Rima et al. (2004) used beetroot fibers for the remediation of water contaminated by heavy metals with a retention percentage attending 97% for some metals. Han (1999) used the lignocellulosic of Kenaf, alfalfa, pinyon juniper, and aspen fibers for filtering toxic heavy metals from storm water.

The chemical modification of lignocellulosics is defined as a chemical reaction between some reactive part of a lignocellulosic and a simple single chemical reagent, with or without a catalyst, to form a covalent bond between the two. This excludes all simple

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chemical impregnation treatments which do not form covalent bonds.

There are several approaches to chemically modifying the lignocellulosic cell wall polymers. The most abundant single site for reactivity in these polymers is the hydroxyl group and most reaction schemes have been based on the reaction of hydroxyl groups. Our objective in this paper is to study the modification of bagasse fibers by ethylenediaminetetraacetic acid (EDTA) salts in order to increase the potential retention of the total dissolved solids (TDSs) of cooling tower water by the modified fibers.

Experimental Setup

Material

The percentage averages of the different components of bagasse fibers are, respectively, 25% of cellulose, 5% of lignin, 30% pectin, and 40% hemicelluloses (Dinand et al. 1996). Bagasse was collected from Big Inland (Hawaii) via the University of Hawaii (UH) agriculture department and cut into small pieces, air-dried, and powdered in a grinder. The meal obtained was first sieved through a 1,000-μm mesh and then through 850, 450, 250, 180, and 100 μm. The fiber powder was soaked in distilled water for 24 h at room temperature and air dried then stored for use. All reagents used for the preparation of solutions were of analytical grade. EDTA disodium salt, $CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 6H_2O$, $Pb(NO_3)_2$, $ZnCl_2$, and $HCl(aq)$ were purchased from Prolabo and used without further purification. Cooling tower water which contains salts (such as chlorine, sulfate, and carbonate) and metal ions (such as iron, copper, and manganese) was collected from three sites in Honolulu. The TDS concentration of cooling tower water and the pH values depend on its original sources and on the cycle number of circulations inside the building. The TDS values change from 300 to 1,200 ppm.

Instruments

The metals were analyzed by atomic absorption spectrometry (Perkin Elmer 5000 and Shimadzu A-6800). The conductivity meter was of ELE Paqualab Type 50. The infrared (IR) spectrum was recorded on a Fourier transform infrared (FTIR) spectrometer (UNICAM). The pH values were measured with a WTW pH/mV Hand-Held Meter 330/SET. The pH meter was calibrated by using pH-buffer solutions.

Preparation of the Modified Fibers

50 g of fibers were transferred into a beaker containing 500 ml of aqueous EDTA sodium salt solution at different concentrations (5, 7.5, 10, 12.5, 17.5, 20, and 25%). The mixture was then heated at 50°C and agitated for 4 h. After filtration the fibers were washed by distilled water several times then dried at 100°C for 24 h.

Column Procedures to Remove TDS and Heavy Metals

The column consisted of a Plexiglas tubing (30-cm height, φ 4.0 cm) perforated at the bottom and connected to a pumping system. In order to assure the homogeneity and reproducibility of the results, the column was filled by 30 g of 1,000-μm fibers. The material was compressed inside the column to reach a density of 0.4 g/cubic centimeter. The flow rate of liquid was 4 GPM (gallons per minute) at a pressure of 15 psi. Also, we proceeded with

the passage of 50 mL of solution through the biomass filter and we have made about 10 passages from the same initial solution to study the saturation of fibers by metal cations.

Heavy metal solutions of different concentrations (1,000, 200, and 100 ppm) were prepared. The pH values were adjusted by the addition of aqueous HCl.

Results and Discussions

The natural fibers contain several chemical functions such as hydroxyl, carboxylic, aldehyde, ketone, and C=N as shown in the FTIR of the fibers in Fig. 1. These chemical functions will play an important role in the grafting of EDTA molecules and the subsequent complexation of metal ions on the surface of fibers.

Effect of pH on the Retention Efficiency

In order to study the effect of pH on the retention efficiency of the modified fibers, we have prepared for each metallic cation, Pb, Cu, and Zn, several solutions at the same concentration (200 ppm) but different pH values varying from 1.5 to 7. Also we tested the retention efficiency for cooling tower water diluted to a TDS value of 100 ppm (Fig. 2).

It is obvious that metallic cations are more easily removed when the pH value increases. The percentage of retention regularly increased to reach a maximum at pH 6.5 with the following values: 100% for lead; 99% for zinc; 98% for copper; and 99% for TDSs in cooling tower water.

Retention Efficiency of Modified Fiber for a Model Solution

The modified fibers were first tested to remove some metallic cations from a model solution containing different cations. This model solution was a mixture of lead, zinc, nickel, and copper cations. The total concentration was 200 ppm (50 ppm of each). Fig. 3 shows that after 10 passages, the retention efficiency of the modified fiber varied from 100 to 96% for lead, 99 to 96% for zinc, 99 to 85% for copper, and from 99 to 77% for nickel. Since the new modified fiber proved its capacity to remove different heavy metals, direct additional tests for the removal of metal ions from cooling tower water were performed.

Retention Efficiency of Modified Fiber for Cooling Tower Water

The same experiment described in the previous section was performed to treat cooling tower water. Fig. 4 shows that for the EDTA-modified bagasse fibers, the average retention efficiency has increased 1.7 times more than that for the unmodified fibers. This result clearly shows the superiority of this new modified material.

Effect of the EDTA Concentration on the Retention Efficiency for Cooling Tower Water

Different concentrations of EDTA salt solutions were used to prepare several types of bagasse modified fibers. The EDTA salt solutions used were at 5, 7.5, 10, 12.5, 15, 17.5, 20, and 25% w/w of EDTA/water. Once these fibers were chemically modified, we studied the retention efficiency of the resulting fiber powder.

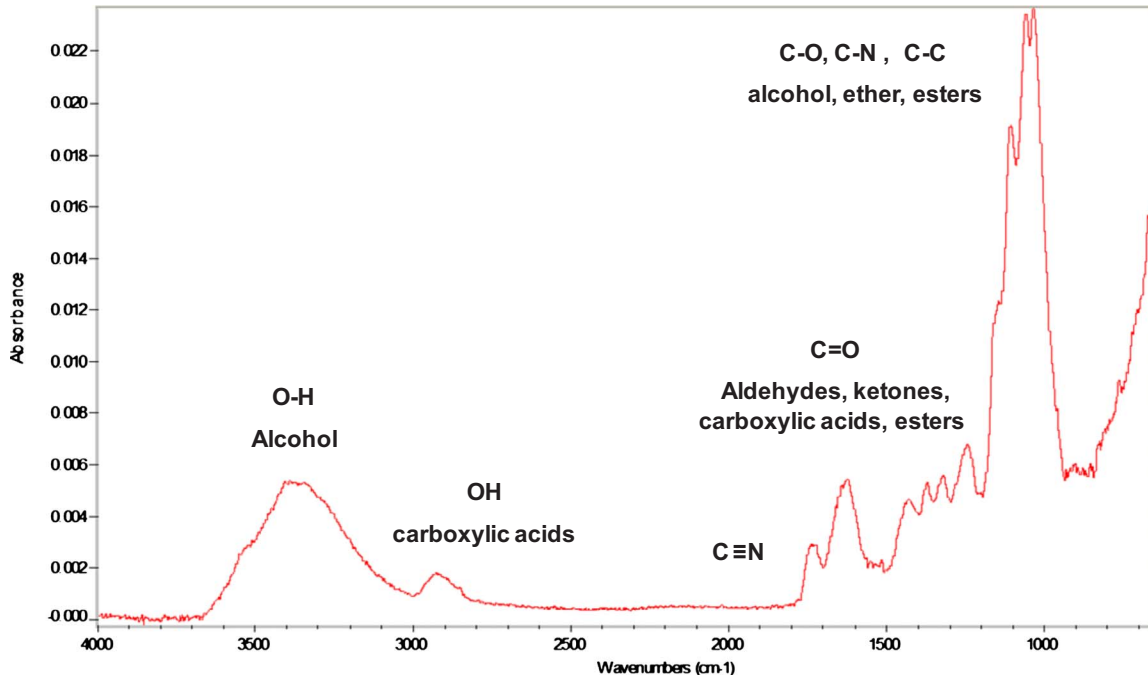The retention results for these different EDTA-modified fibers

Fig. 1. FTIR spectrum of bagasse fiber showing different chemical functions

are shown drawn in Fig. 5. According to this figure, when the concentration of the EDTA salt solution used for the modification of bagasse fibers increases from 5 to 25%, the retention efficiency of the modified fiber increases from 8.5 to 29.5 mg/g of fiber.

Effect of the Fiber Size on the Retention Efficiency for Cooling Tower Water

In order to study the effect of the fiber size we tested different fiber sizes as prepared according to the above description. In all these experiments we saturated the column filter and then we estimated the maximum mass of the retained TDS. Fig. 6 shows the evolution of the retention efficiency for modified and unmodified bagasse fibers. The results show that the maximum of retention can reach 60 mg/g of unmodified material and 78 mg/g of

EDTA-modified fiber. At $1,000$ μm as particle size, the removal efficiency of unmodified bagasse fibers was about 14–15 mg/g. This result is similar to the retention efficiency previously obtained using beetroot fibers (Rima et al. 2004).

Adsorption Isotherms

Two important physiochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibria of the adsorption and the kinetics. Equilibrium studies give the capacity of the adsorbent. The equilibrium relationships between the adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in
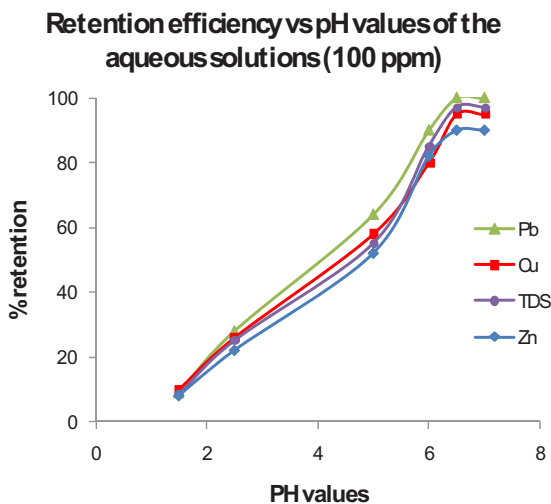

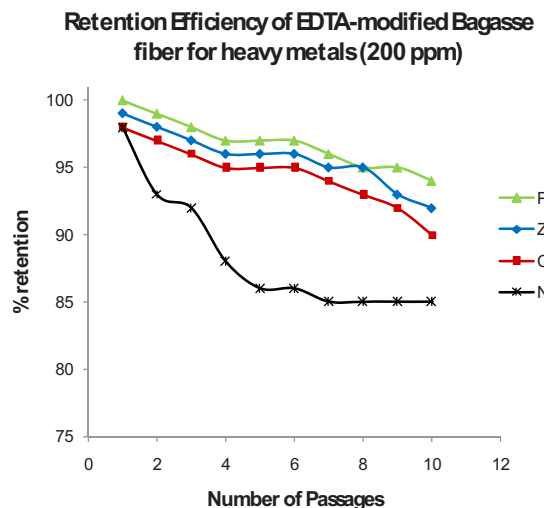**Fig. 2.** Retention efficiency of different cations at different pH values

Fig. 3. Retention efficiency of modified fiber for a model solution

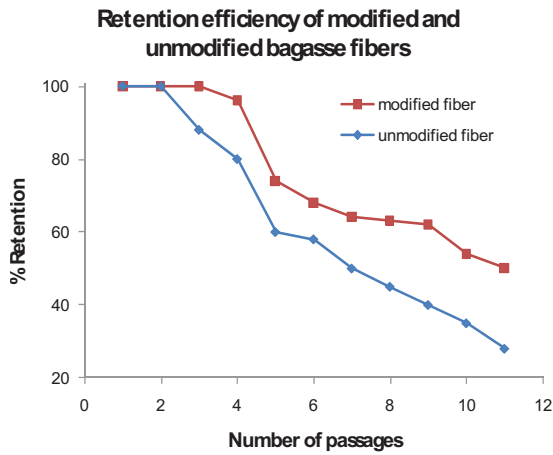**Retention efficiency of modified and unmodified bagasse fibers**

Fig. 4. TDS removal from cooling water by modified and unmodified fibers

the solution at a fixed temperature at equilibrium. There are two types of adsorption isotherms: Langmuir adsorption isotherms and Freundlich adsorption isotherms.

Langmuir Isotherm
The Langmuir adsorption isotherm is often used for the adsorption of a solute from a liquid solution. The Langmuir adsorption isotherm is often expressed as

$$Q_e = X_m K C_e / (1 + K C_e)$$

where Q_e=adsorption density at the equilibrium solute concentration C_e (milligrams of adsorbate per gram of adsorbent); C_e=concentration of the adsorbate in the solution (mg/L); X_m=maximum adsorption capacity corresponding to complete monolayer coverage (milligrams of solute adsorbed per gram of adsorbent); K=Langmuir constant related to the energy of adsorption (liters of adsorbent per milligram of adsorbate).

The above equation can be rearranged to the following linear form:

$$C_e/Q_e = 1/X_m K + C_e/X_m$$

The linear form can be used for the linearization of experimental data by plotting C_e/Q_e against C_e. The Langmuir constants X_m
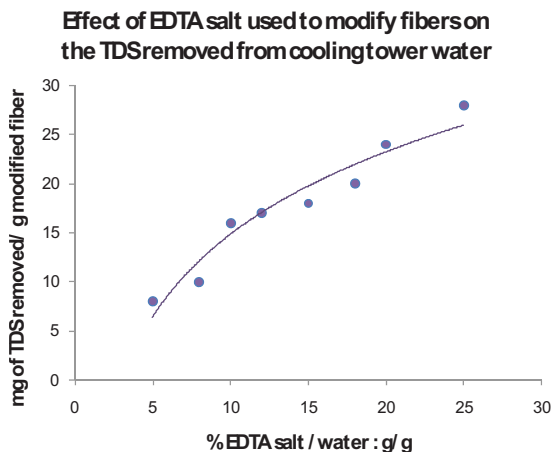
Effect of EDTA salt used to modify fibers on the TDS removed from cooling tower water

Fig. 5. Effect of EDTA salt used on the TDS removal from cooling tower water

Effect of the fiber size on the Retention efficiency for TDS (Fiber modified by EDTA 10%)
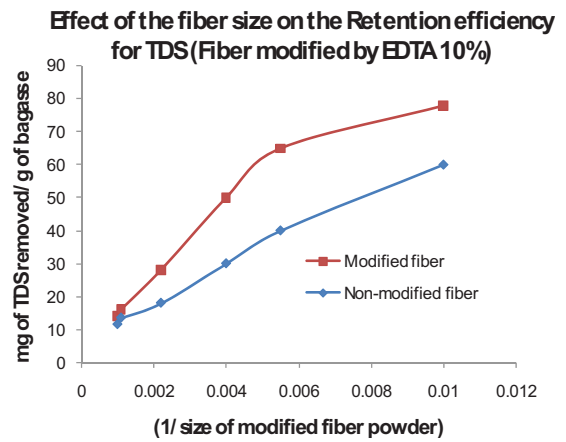

Fig. 6. Effect of the fiber size on the TDS removal from cooling tower water

and K can be evaluated from the slope and intercept of the linear equation.

Freundlich Isotherm
The Freundlich isotherm is the relationship describing the adsorption equation and is often expressed as

$$Q_e = K_f C_e^{1/n}$$

where Q_e=adsorption density (milligrams of adsorbate per gram of adsorbent); C_e=concentration of the adsorbate in solution (mg/L); K_f and n=empirical constants dependent on several environmental factors and n is greater than 1.

This equation is conveniently used in the linear form by taking the logarithmic of both sides as

$$\ln Q_e = \ln Kf + 1/n \ln C_e$$

A plot of $\ln C_e$ against $\ln Q_e$ yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constants can be determined from the slope and the intercept.

Method Used for Adsorption Test
The method used for the adsorption tests for different TDS concentrations is as follows:
- 10 g of fibers as an adsorbent were transferred into a column and different concentrations of hard water were filtered through the column.
- For each concentration, the hard water was filtered through the modified fiber several times until complete saturation of the filter fiber. The water TDS values that have been tested were 1,000, 850, 750, 600, and 400 ppm.
- Q_e was determined and C_e/Q_e versus C_e and $\ln Q_e$ versus $\ln C_e$ were plotted.

The Langmuir constant X_m (maximum adsorption capacity) and the Freundlich constant K_f were obtained from the linear equations. The values are summarized in Table 1. The Langmuir and Freundlich plots are presented in Figs. 7(a and b), respectively.

For both isotherm models we observed that the estimated adsorbed quantities of the minerals are fitted. Fried et al. (1977) and Igwe and Abia (2006) studied the adsorption isotherms of biosorbents to remove the heavy metals from wastewater. They classified the adsorption isotherm into six types of adsorption. Microporous adsorbents produce adsorption isotherms of Type 1 (which has a convex shape) and it is also associated with mono-

Table 1. Langmuir and Freundlich Constants

Cooling tower water	Langmuir isotherm constants			Freundlich isotherm constants		
	X_m (mg/g)	K (L/mg)	R^2	K_f	$1/n$	R^2
Hard water	76.9	0.0031	0.9974	1.35	1.36	0.9987
Equations		$y = 0.0134x + 4.1277$			$y = 0.7311x + 0.3042$	
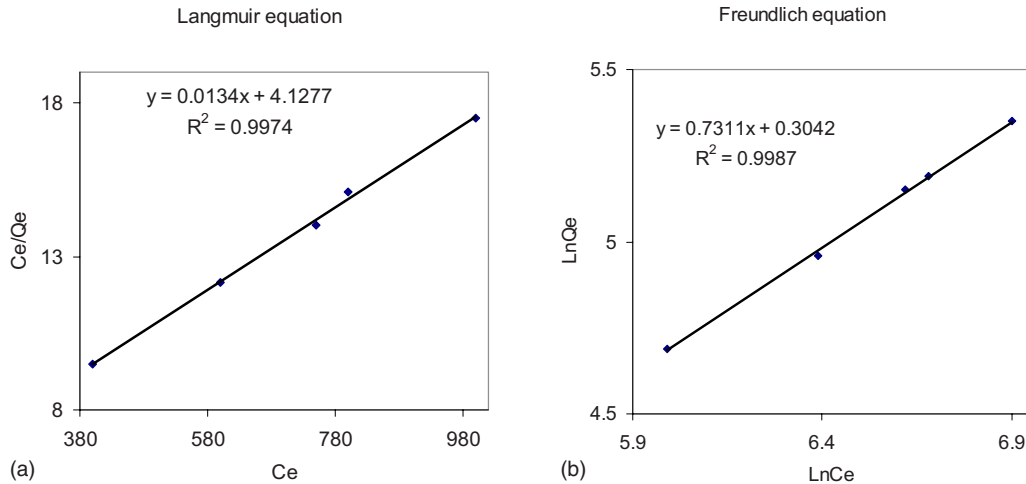
Fig. 7. (a) Langmuir adsorption isotherm; (b) Freundlich adsorption isotherm

molecular layer adsorption. Types II and III depict adsorption for multimolecular layer formation while Types IV and V describe the adsorption process of multimolecular layer formation and condensation in pores. Type VI represents the surface phase transition of a monomolecular layer on a homogeneous surface (Igwe and Abia 2006). The applications of the Freundlich and Langmuir models were used to show the favorable elimination of heavy metals from the wastewater.

Conclusion

In this study, unmodified and EDTA-modified bagasse fibers have been tested for the removal of TDSs from cooling tower water. The modification of fibers using EDTA has been shown to enhance the removal capacity compared to the unmodified fibers. The removal of TDSs from cooling tower water is highly pH dependent and the best results were obtained at pH 6.5. The removal efficiency was found to increase significantly with the percentage of EDTA attached to the fiber and with the decrease of fiber size. The modified bagasse fibers presented a higher efficiency compared to both the unmodified bagasse and beetroot fibers as previously described (Rima et al. 2004).

The regeneration of fibers is one of our perspective works because the preliminary results showed that by modifying the pH the ions retained by the fiber can be released. Also, it is important to mention that the saturated fibers can be treated by a biodegradation process. This is the reason for why we used the natural fibers as remediation technology.

The isotherms of both Freundlich and Langmuir were established and they described the removal process indicating favorable elimination of minerals from cooling tower water. This removal mechanism involves either complexation by chemical

functions of fibers or adsorption by electrostatic van der Waals interactions.

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