Surface Modification of Celluloses Extracted from Oil Palm Empty Fruit Bunches for Heavy Metal Sorption

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Contamination of environment with heavy metals such as cadmium, cobalt, copper, nickel and manganese is becoming a major problem due to their toxicity persistency and bioaccumulation tendency. Cellulose fibers extracted from Oil Palm Empty Fruit Bunches (OPEFB) were surface modified using esterification method with Acetic acid and Ethylenediaminetetraacetic acid (EDTA) for sorption of heavy metals such as copper, nickel and manganese from water. The effects of metal ion concentrations (100 – 1000 ppm), initial pH (4-8) of metal solution and contact time (15min-3h) on sorption capacity were studied. EDTA-modified cellulose showed better adsorption capacity due to the existence of four carboxylic acid groups that capture the metal ions. Increasing pH value and metal ion concentration also resulted in increased sorption.

1. Introduction

Water pollution and its remediation is one of the major challenges faced by the world today. Contamination of water with heavy metal ions such as cadmium, cobalt, copper and nickel released into the environment from activities such as electroplating plants, mining, metal finishing, welding and alloy, is posing serious threat to the public health due to their toxicity persistency and bioaccumulation tendency in nature (Kumar et al., 2013). Heavy metals are not biodegradable and cannot be metabolized or decomposed, unlike some organic pollutants. Entrain of this material into the food chain through a number of pathways cause toxic effects in organisms over their life span. In the long-term, even chronic low-grade toxicity may be more damaging and hazardous to health (Sud et al., 2008).

Many different methods for heavy metal removal have been applied including chemical precipitation, chemical oxidation/reduction, reverse osmosis, electrodialysis and ultrafiltration from aqueous solutions, but these methods have low efficiency, high cost and generate toxic wastes. Adsorption is attractive because of its simplicity, convenience and efficiency. Biosorbents from renewable sources are economical and biodegradable, and have potential for industrial applications (Li et al., 2011, McManamon et al., 2012). Eco-friendly extraction of cellulose from OPEFB has been reported (Nazir et al., 2013). Cellulose is one of the most abundant renewable polymers that can be surface engineered to develop biosorbent with durable properties to capture heavy metals.

In this work, cellulose from OPEFB was surface modified with acetic acid and EDTA to remove copper, nickel and manganese ions from water. The effects of initial pH, contact time and metal ion concentration were investigated.

2. Materials and Methods

2.1 Modification of Cellulose
Modification of cellulose were done by esterification method with two reagents containing carboxylic acid groups - EDTA (4 COOH groups) and acetic acid (1 COOH groups). Twenty grams of dried mercerized cellulose (treated in NaOH solution) was placed in round bottom flask and 200 mL of acetic acid (10% wt) was added (1:10 ratio). The solution was refluxed for 2 hours at 100°C and filtered and dried. The same procedure was carried out for EDTA solution.

2.2 Preparation of metal ions stock solution
To simulate typical aqueous solutions containing Cu^{2+}, Ni^{2+} and Mn^{2+} ions, stock solutions were prepared from $CuSO_4$, $NiCl_2$, and $MnSO4$. Stock solution of each salts at 1000 ppm was prepared and the different concentrations (100 - 1000ppm) were obtained by serial dilution to study the effects of initial metal concentration on adsorption efficiency. For the effects of initial pH (4-8) of metal solution, pH was adjusted with diluted CH_3COOH (0.01 M) or NaOH (0.01 M). The effects of equilibrium contact time (10-150 min) were also determined.

2.3 Batch adsorption
Batch adsorption studies were carried out by mixing 0.5 g of treated cellulose with 50 mL of aqueous metal ions at different concentrations, pH and contact time. The solution–adsorbent mixtures were stirred at 140 rpm, and at the end of pre-determined time interval, the reaction mixtures were filtered out and analyzed by Polarized Zeeman Atomic Adsorption Spectrometer. The amount of metal ions adsorbed at equilibrium, q_e (mg/g) was calculated based on Eq (1):

$$q_e = \frac{(C_o - C_e) \times V}{W} \tag{1}$$

where C_o and C_e are the initial and equilibrium metal ion concentrations (mg/L), respectively, V is the volume of metal ion solution (L), and W is the weight of biosorbent (g).

2.4 Kinetic study
Pseudo second-order kinetic model was used to evaluate the adsorption kinetics data (Taty-Costodes et al., 2003):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

where q_t (mg/g) is the amount of the adsorption at time t (min) and k_2 (g/mg/min) is the constant of the pseudo second-order kinetic model. The graphs of t/q_t versus t were plotted to determine the fitness and estimate the kinetics constants.

2.5 Adsoprtion Isotherms
Adsorption isotherms explain the ratio between the amounts of ion adsorbed and remaining in the solution to obtain the adsorbent capacity and the equilibrium relationships between adsorbent and adsorbate. Freundlich and Langmuir isotherms are the most frequently used models (Jalali et al, 2002), and Dubinin-Radushkevich isotherm model is used for comparison. Langmuir model estimates maximum adsorption capacity related to complete monolayer soprtion on the adsorbent surface and often for a homogeneous system, while Freundlich isotherm model describes a more heterogeneous sorption to estimate the adsorption intensity of the sorbate towards the adsorbent. Dubinin-Radushkevich isotherm model estimates the characteristic porosity of the adsorbent and the apparent energy of adsorption.

2.5.1 Freundlich isotherm. The Freundlich isotherm model is described as follows:

$$q_e = K_F (C_e)^{1/n} \tag{3}$$

where, K_F and n are the Freundlich empirical constants (Tengs and Hsieh, 1998). The linearized form is used for data analysis:

$$log\ q_e = log\ K_F + 1/n\ log\ C_e \tag{4}$$

where, C_e is the equilibrium metal ion concentration (mg/L) and Q_e is the equilibrium amount adsorbed per specified amount of adsorbent (mg/g). The values of K_F (the binding constant) and n, the exponent, determine the steepness and curvature of the isotherm (Akgerman and Zardkoohi, 1996).

2.5.2 Langmuir isotherm. The linearized form of Langmuir equation (Eligwe et al, 1999) is:

$$C_e/q_e = 1/K_L\ b + 1/b\ C_e \tag{5}$$

where *b* (mg/g) is the sorbent binding capacity, representing the required amount of adsorbate to form a monolayer adsorbent surface and K_L is the Langmuir equilibrium constant corresponding to the adsorption/ desorption energy.

2.5.3 Dubinin-Radushkevich isotherm. The Dubinin-Radushkevich isotherm model is expressed as:

$$q_e = q_D \ exp \ (- B_D \ [RT \ ln \ (1 + 1/C_e)]) \tag{6}$$

where, B_D is relevant to the free energy of sorption per mole of the sorbate as coverage to the sorbent surface and q_D is the Dubinin-Radushkevich isotherm constant (Horsfall et al, 2004). The linear form of equation (6) is:

$$ln \ q_e = ln \ q_D - 2B_D RT \ ln \ (1 + 1/C_e) \tag{7}$$

The apparent energy (*E*) of adsorption related to Dubinin-Radushkevich model is calculated as follows (Horsfall et al, 2004):

$$E = \frac{1}{\sqrt{2B_D}} \tag{8}$$

3. Results and Discussion

3.1 Effect of contact time

The effect of contact time on three different metal ions adsorption at 500 ppm initial concentration is shown in Figure 1. Cu ions sorption appeared much higher than other metals. The results follow the order of decreasing relative atomic mass of the three metals ions:- $Cu^{+2} > Ni^{+2} > Mn^{+2}$. After a certain time, the adsorption capacity reached its peak and remained constant, suggesting that the vacant surface sites available at the beginning are fully occupied by solute molecules (Taty-Costodes et al, 2003). The adsorption of manganese ions reached equilibrium after 75 min while nickel and copper reached equilibrium after 90 and 120 min, respectively. The difference can be attributable to the mode of interaction of each metal towards the adsorbent, a result of the difference in atomic weight of metal ions.

3.2 Effect of initial metal concentration

As shown in Figure 2, the amount of metal ions adsorbed per unit mass of adsorbent increased with increasing metal ion concentration from 100 to 1000 ppm. It is to be expected as higher initial metal concentration increases the affinity of metal ions towards the active sites.

3.3 Effect of pH

The effect of different initial pH was evaluated at 500 ppm initial metal concentration and 1 h contact time. The adsorption capacity was low at pH 4, as the high concentration of H^+ may compete with metal ions to occupy the active sites. With increasing pH, the adsorption capacity increased too but to a certain pH value, when the capacity started to be constant and later decline due to excessive diffusion into the active sites at pH above the optimum (Hui et al, 2005). The optimum pH value of Cu^{2+} was 6.5 for EDTA-cellulose sorbent, and pH 7 for acetic acid-cellulose sorbent. For Ni^{2+}, it was 6 for both, Cu^{2+} and for Mn^{2+}, and it was 5.5 and 6, for EDTA and acetic acid sorbent, respectively.
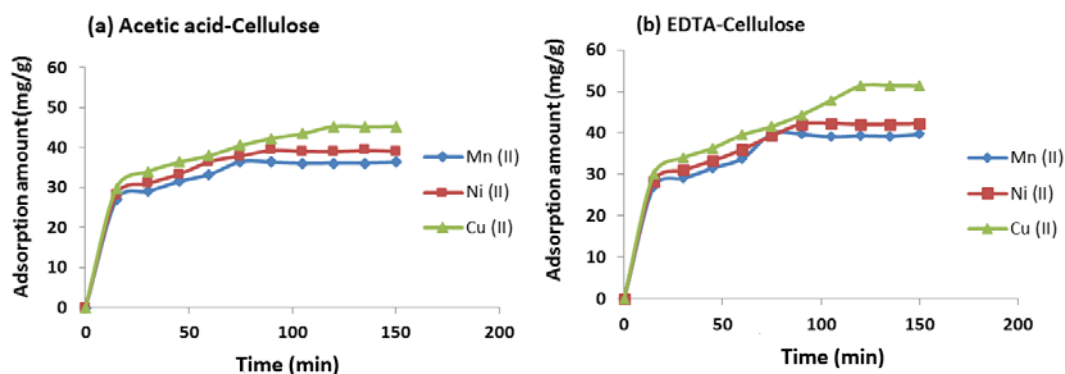

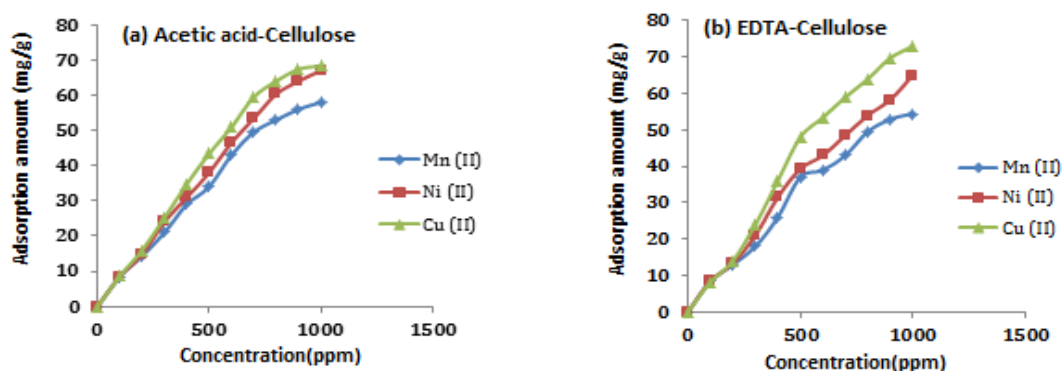*Figure 1: Effect of contact time on metal ion sorption for a) Acetic acid-cellulose, b) EDTA-cellulose*

Figure 2: Effect of initial concentration on metal ion sorption for a) Acetic acid-cellulose b) EDTA-cellulose

3.4 Kinetic study

Both pseudo first order and pseudo second-order rate equation were used to test the kinetic data of related metal ions. However, the first-order model showed low correlation coefficient (R^2) and poor fitting (data not shown). Figure 3 shows that pseudo-second order kinetics model fits the data well. As shown in Table 1, the calculated q_e values for the pseudo second-order model agree well with experimental values where the R^2 values are close to 1. EDTA-modified sorbent only showed slightly better sorption performance than acetic acid.
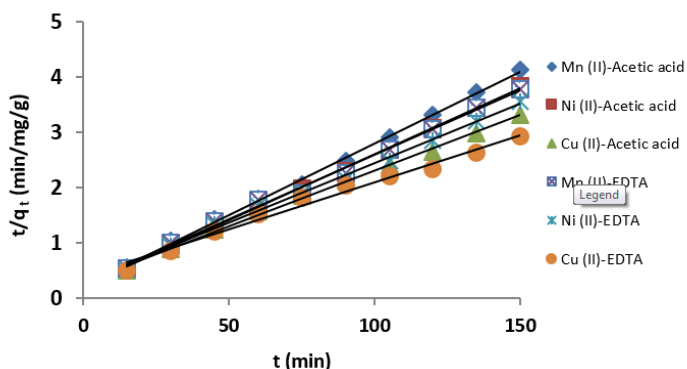

Figure 3: Pseudo second-order kinetic model for metal ion sorption onto surface modified cellulose sorbent

Table 1: Sorption kinetics parameters based on pseudo second order kinetics model

Surface modification	Metal ion	K_2 (g/mg/min)	q_e (mg/g) Model	q_e (mg/g) Experimental	R^2
Acetic Acid	Mn(II)	0.0032	39.61	36.4	0.998
	Ni(II)	0.0021	42.91	39.1	0.995
	Cu(II)	0.0013	49.75	45.3	0.997
EDTA	Mn(II)	0.0021	42.91	39.3	0.995
	Ni(II)	0.0016	46.21	42.1	0.997
	Cu(II)	0.0007	58.83	54.2	0.995

3.5 Adsorption Isotherms

Figure 4 shows the linear plots based on Freundlich isotherm and Figure 5 based on Dubinin-Radushkevich (D-R) isotherm model. As shown in Table 2, both models showed good fitness to the data with $R^2 > 0.8$, where the D-R model mostly showed $R^2 > 0.9$. The Langmuir model however did not describe the data well (plot not shown). The high values of q_D in D-R model suggest high sorption capacity, while the apparent energy of adsorption suggests physisorption process, with high possibility of charge interactions between positively-charged metal ions and negatively-charged carboxylic acids.
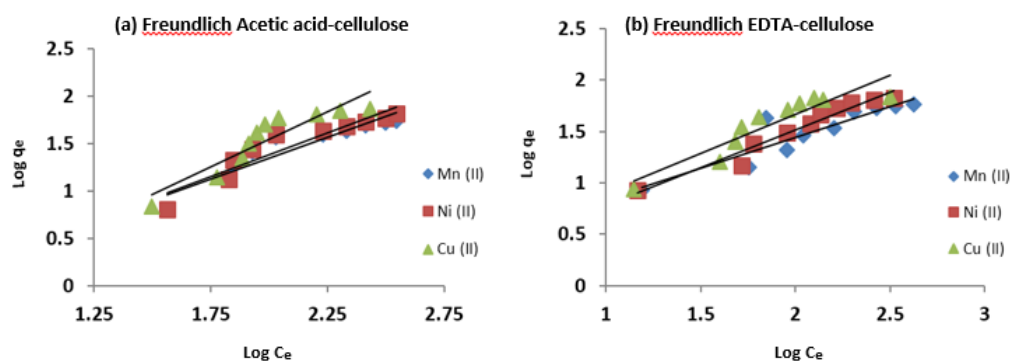
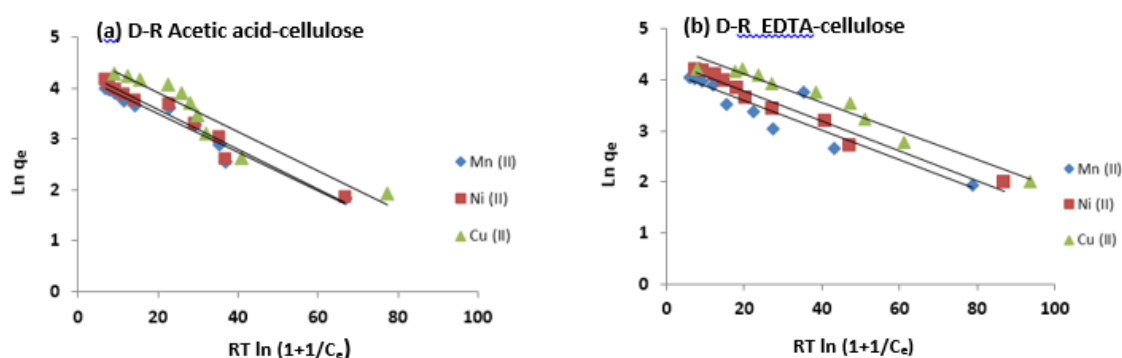Figure 4: Freundlich plot for metal ion sorption onto a) Acetic acid-cellulose, b) EDTA-cellulose sorbents

Figure 5: D-R plot for metal ion sorption onto a) Acetic acid- cellulose, b) EDTA-cellulose sorbents

Table 2: Adsorption isotherms model parameters

Model		Freundlich			Langmuir			D-R			
	Metal ion	K_f	n	R^2	q_m	b	R^2	B_D	q_D	E	R^2
Acetic Acid	Mn	2.59	1.13	0.876	0.003	96.15	0.643	0.019	60.26	5.129	0.918
	Ni	2.88	1.08	0.883	0.003	113.63	0.626	0.019	79.83	5.050	0.963
	Cu	2.57	0.85	0.846	0.005	131.57	0.291	0.019	87.70	5.103	0.904
EDTA	Mn	3.98	4.14	0.834	0.004	87.71	0.796	0.014	64.34	5.892	0.855
	Ni	5.43	5.46	0.958	0.003	131.57	0.755	0.014	87.00	5.842	0.966
	Cu	5.74	6.72	0.851	0.007	106.38	0.748	0.014	90.13	5.954	0.964

4. Conclusion

Cellulose extracted from OPEFB had been successfully surface-modified with acetic acid and EDTA to be used as biosobent for heavy metal removal from water. High adsorption capacity was achieved for the removal of Mn (II), Ni (II) and Cu (II) ions from aqueous solutions at optimum condition. EDTA surface modification showed slightly better sorption capacity than acetic acid. The sorption followed pseudo second-order kinetics model and best described by Dubinin-Radushkevich isotherm model.

Acknowledgments

References

Akgerman A., Zardkoohi M., 1996, Adsorption of phenolic compounds on fly Ash. J. Chem. Eng. Data, 41, 185-187.

Eligwe C.A., Nwoko C.I.A., Egerreonu U.U., 1999, Adsorption properties of Dextrin onto modified Hematite surfaces. J. Chem.Soc. Nigeria, 24, 70-76.

Ghimire K.N., Inoue K., Ohto K., Hayashida T., 2007, Adsorptive separation of metallic pollutants onto waste seaweeds, *Porphyra yezoensis* and *Ulva japonica*. Sep.. Sci. Tech, 42, 2003–2018.

Horsfall M.J., Spiff A.I., Abia A.A., 2004, Studies on the influence of mercaptoacetic acid (MAA) modification of cassava (manihot sculenta cranz) waste biomass on the adsorption of Cu^{2+} and Cd^{2+} from aqueous solution. Bull. Korean. Chem. Soc, 25, 969-976.

Hui K.S., Chao C.Y.H., Kot S.C., 2005, Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash. J.Hazard. Mater. 127, 89–101.

Jalili R., Ghafourian H., Asef Y., Davarpanah S.J. Sepehr S., 2002, Removal and recovery of lead using nonliving biomass of marine algae. J. Hazard. Mater, 92, 253-262.

Kumar R., Barakat M.A., Daza Y.A., Woodcock H.L., Kuhn J.N., 2013, EDTA functionalized silica for removal of Cu(II), Zn(II) and Ni(II) from aqueous solution.J. Colloid Interface. Sci. 408, 200-205.

Li S., Yue X., Jing Y., Bai S., Dai Z., 2011, Fabrication of zonal thiol-functionalized silica nanofibers for removal of heavy metal ions from wastewater. Colloids. Surf. A, 380, 229–233.

McManamon C., Burke A., Holmes J.D., Morris M.A., 2012, Amine-functionalised SBA-15 of tailored pore size for heavy metal adsorption. J. Colloid Interface Sci. 369, 330–337.

Nazir M.S, Wahjoedi B.A., Yussof A.W., Abdullah M.A., 2013, Eco-friendly extraction and characterization of Cellulose from Oil Palm Empty Fruit Bunches, Bioresour. 8(2), 2161-2172.

Sud D., Mahajan G., Kaur M.P., 2008, Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions. A review. Bioresour. Tech. 99(14), 6017–6027.

Taty-Costodes V.C., Fauduet H., Porte A.C., 2003, Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of Pinus sylvestris. J. Hazard. Mater. 105, 121–142.

Teng H., Hsieh, C.T., 1998, Influence of surface characteristics on liquid-phase adsorption of phenol by activated carbons prepared from bituminous coal. Ind. Eng. Chem. Res. 37, 3618-3624.