Egypt. J. Chem. **Vol. 64,** No. 4 pp. 1701 - 1708 (2021)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Selective Separation of Cu(II) from A single Metal Ion Solution by Using O-amino thiophenol-modified flax fiberd

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Abstract

Newly synthesized ortho-amino thio-phenol modified flax fibers (OATP-MFF) were prepared in two subsequent steps; at first flax fiber was pretreated with potassium periodate. Then, the pretreated fibers were condensed with ortho-amino thio-phenol to form the modified flax fibers(OATP-MFF). The OATP-MFF were characterized by (FTIR) Fourier transform infrared spectra, SEM and energy-dispersive X-ray Spectroscopy (EDX). The newly synthesized OATP-MFF chelating fibers were utilized for selective separation of Cu(II) from aqueous solution by adsorption methodology. The effects of pH, the initial concentration of metal ions, the adsorbent dosage, the interfering ions and the contact time on the adsorption capacity of OATP-MFF chelating fibers were investigated. The maximum adsorption capacity of Cu(II) at the optimum conditions was 92 mg/g. The adsorption process fitted well the second-order model kinetic of. The chemical (adsorption) reaction is the rate-limiting step that was proved from the kinetic model.

Keywords: O-amino thiophenol; flax fiber; Cu (II); single metal ion solution.

1. Introduction

Currently, providing pure water for consumption by humans has an important and a big concern in the whole world because of the direct effects on the environment and human health that water causes. Heavy metals' pollution is very dangerous because of its bad impacts on living organisms as human health and life fields as agriculture because it precipitates in the body at vital organs such as liver, bone, and kidney. So their removal is a vital matter because the exposure to them has harmful effects on human health like cardiovascular disorders and cancer. Heavy metals occurred in the environment either normally or because of human actions [1-3].

Separation methods like membrane filtration, chemical precipitation, solvent extraction and ion exchange techniques, etc. , are utilized to get rid of these pollutants. Yet, these techniques are not adequate to be utilized in the removal of low metal concentrations. Adsorption technique is considered a suitable method that can be utilized for removal of low concentrations of these pollutants from wastewater because it has a lot of advantages like cheapness and ease of operation [4]. Many adsorbents such as cellulose, chitosan and active carbon have been utilized for heavy metals removal [5-23]. Chelating fibers have been widely used to separate and remove toxic heavy metals from many contaminated solutions because of their high adsorption capacity and selectivity [24-26]. Cellulose enters in the composition of plant fibers and is considered as the most plentiful natural polymer in the world. Modification of cellulose can be done by chemical or physical methods. Chemical modifications is very significant as it enhances the cellulose adsorption capacity and the ability for removing heavy metals from aqueous media Chemical modification of cellulose maybe done by using acids, organic compounds, bases or minerals. [27-29]. The oxidation of the cellulose by a selective oxidizing agent like periodate is very important as the resultant dialdehyde cellulose has great ability to be modified with many functional groups as aliphatic or aromatic amines.

In the present study, flax fibers are modified using a cheap ligand to obtain ortho-amino thiophenol modified flux (OATP-MFF). The newly prepared OATP-MFF has been successfully used for selective adsorption of Cu(II) from aqueous solutions. The different experimental variables affecting the adsorption process were thoroughly investigated viz. pH, initial concentration of Cu(II) ions, dosage of adsorbant, contact time and temperature.

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Receive Date: 18 November 2020, Revise Date: 04 December 2020, Accept Date: 29 December 2020
DOI: 10.21608/EJCHEM.2020.50297.3029

2. Materials and methods

2.1. Materials

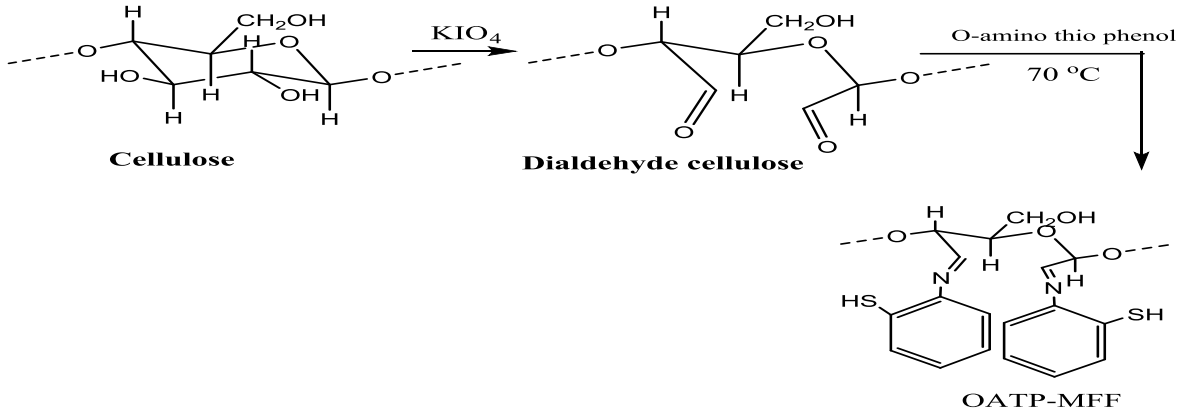
Flax fibers were obtained from Tanta flax and Oil Company. Potassium periodate, O-amino thiophenol and $CuCl_2.2H_2O$ were purchased from Sigma Com.

2.2. Instrumentation

The infra-red spectra of the oxidized cellulose and OATP-MFF fibers were recorded utilizing Fourier transform infra-red spectroscopy(FTIR) utilizing KBr discs. A Perkin-Elmer flow injection system (FIAS-400) has been utilized with an AS-90 autosampler and a Perkin-Elmer 4100 ZL Atomic Absorption Spectrometer. EDX analysis of OATP-MFF was done by utilizing a(JSM-6510LV). The morphological structures of oxidized cellulose and OATP-MFF were determined using SEM (FEI Quanta-200 FEI Company, The Netherlands).Gold was used for samples coating before SEM analysis.

2.*3. Preparation of the OATP-MFF*

The O-amino thiophenol -modified flax fiber (OATP-MFF) was prepared in two steps. Firstly, 1 gram of flax fibers was put with 100 ml of 4% KIO4 aqueous solution and the mixture was shaken for 60 minutes at temperature 50 ºC in complete absence of light to give dialdehyde form of cellulose [30]. In the second step, refluxing and condensation of the prepared dialdehyde-flax fiber cellulose was performed using 0.2 L alcoholic O-amino thiophenol 2% (W/V) for four hours at 70ºC as reaction temperature, in the presence of 0.5 ml tri-ethylamine [31]. The synthesis of (OATP-MFF) is schematically represented in scheme 1.



Scheme1: Synthesis of OATP-MFF

2.4. Metal ion adsorption and elution experiments

The adsorption experiments were performed by putting 0.05 gram of OATP-MFF material with 50 ml of Cu(II) solution in 100 ml stoppered glass bottles with initial concentration (50, 100, 150, 200, 250, 300, and 350 ppm). The effect of pH was studied at (1- 6) and the temperature effect was studied at (20ºC- 40ºC). The kinetics of the adsorption process were studied at time intervals (30-140 min) and at 150 rpm as a constant rate to all bottles. After the shaking, filtration of the OATP-MFF was performed. The residual Cu(II) in the filtrate was measured by FAAS at λ_{max}= 324.8 nm. The removal efficiency(R,%) of OATP-MFF was calculated from equation(1)

. (R %) = (Ci-Ce) /C_i x 100 Eq. (1)

The maximum capacity (q_e) of OATP-MFF was calculated from equation (2)

$$qe = \frac{(Ci - Ce) * V}{W} \qquad \text{Eq. (2)}$$

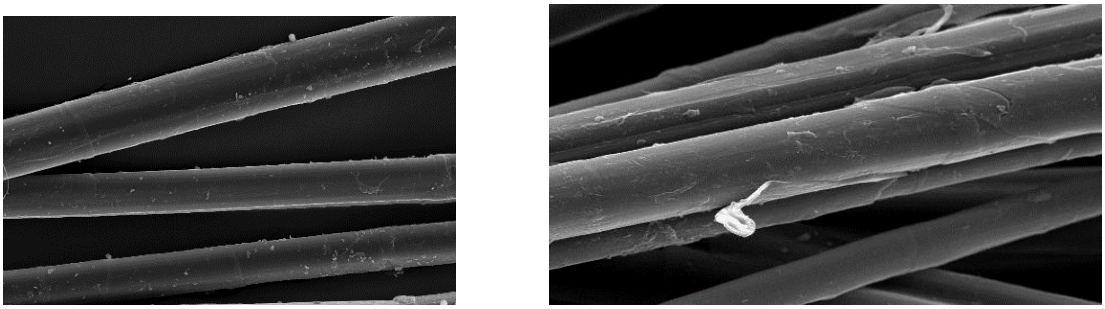
Where R % is the removal percent; C_i and Ce are the initial metal concentration and the concentration at equilibrium (mg L^{-1}), respectively. qe (mg/g), w (gram) and V (L) are the adsorption capacity, weight of dry sorbent material, and solution volume, respectively.

3. Results and discussion

3.1. Characterization

3.1.1. Scanning electron microscopy (SEM)

The changes in the morphological structure for the oxidized flax fiber and OATP-MFF were detected using SEM ((Figure 1(a, b)). The presence of both rough and tight strips on the surface of the oxidized flax fiber may be due to oxidation action on the flax fibers (Fig. 1a). The roughness disappeared after treatment of oxidized cellulose by ortho-amino thio-phenol due to insertion of ortho-amino thio-phenol in the pores of the oxidized one ((Fig.(1b)).



(a) (b)

Fig. 1. SEM photos of (a) oxidized cellulose, (b) OATP-MFF

3.1.2. Infrared spectra

Preparation of OATP-MFF was confirmed by the FT-IR spectra of the oxidized cellulose and OATP-MFF. The IR spectra of native flax fibers(Fig. 2) shows peaks at about 1070 cm^{-1} - 1150cm^{-1} that may be due to C-O stretching vibrations, 1250cm^{-1} - 1420cm^{-1} due to O-H bending vibrations and 3500cm^{-1} - 3200cm^{-1} because of O-H stretching vibrations. The spectrum of dialdhyde cellulose in (Fig.3 (a)), after oxidation by periodate is confirmed by the appearance of a peak at 1730cm^{-1}, which is interconnected with stretching vibrations of aldehyde group [32]. After reaction of the ortho amino thio-phenol with dialdehyde cellulose, the IR spectrum of the prepared OATP-MFF in (Fig.3(b)) shows the appearance of new peaks at about 1690cm^{-1} which may be interconnected with Schiff base azo-methane group that is formed between the dialdehyde groups of the oxidized flax fibers and ortho amino thio-phenol.

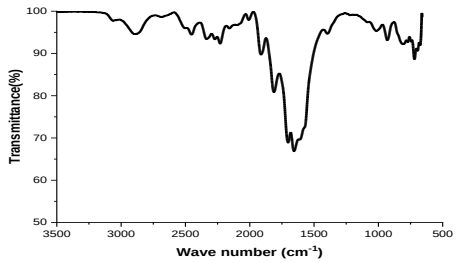


Fig.2. FTIR spectra of native cellulose

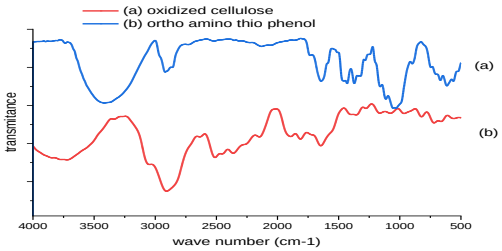


Fig. 3. FTIR spectra of (a) oxidized cellulose and (b) OATP-MFF

3.1. 3. Energy dispersive X-ray spectroscopy (EDX)

When an atom was struck by a beam of an incident electron, it may cause an inner shell electron ejection. If the electron beam has sufficient energy. Then the energy is released in Auger electron or X-ray photon forms. When the excited atom returns back to its stable state. Each atom has its specific X-ray emission energy so that EDX provides the sample's chemical information. As it can be seen in Fig. 4 the sulfur peak can be detected on the surface of OATP-MFF beside N, C, and O principal peaks.

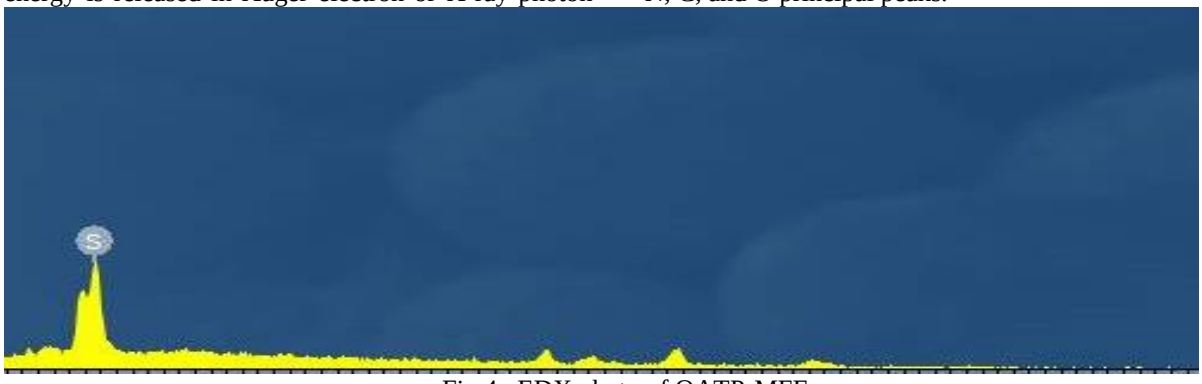


Fig.4. EDX photo of OATP-MFF

3.2. Influence of pH

It was previously stated that metal ions adsorption from aqueous solution is strongly affected by pH [33]. The pH was studied in a range from pH 1 to 6 by using acetate buffer. As shown in Fig. 5, Cu^{+2} ions adsorption increased by increasing pH value. The maximum adsorption for copper ions was achieved at pH 6. The uptake of Cu^{+2} ions takes place by coordination with OATP-MFF active sites. At low pH, the competition occurs between H^{+} and Cu^{+2} ions because of protonation of active sites which causes lowering these positions ability for taking the studied metal ions.

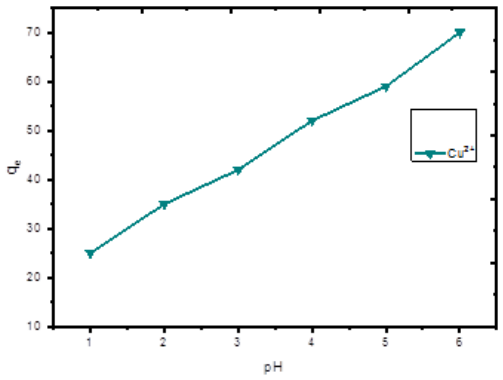


Fig. 5. pH effect on Cu(II) adsorption on OATP-MFF surface

3.3. Influence of temperature on adsorption capacities

Different parameters such as (ΔH^{o}_{ads}), (ΔG^{o}_{ads}) and (ΔS°_{ads}), heat of enthalpy, standard free energy and entropy of adsorption using OATP-MFF were determined for metal ions adsorption at various temperatures in the range 20 oC – 40 oC. The thermodynamic equilibrium constant was calculated such as:

$$K_C \frac{C_{ads}}{C_e} \qquad \text{Eq (3)}$$

$$\Delta G^{o}_{ads} = -RT \ln K_C \qquad \text{Eq (4)}$$

$$\ln K_C = (\Delta S^{o}_{ads} / R) - (\Delta H^{o}_{ads} / RT) \qquad \text{Eq (5)}$$

Where C_{ads} and C_e are the sorbed metal ions concentration (mg. g^{-1}) by (OATP-MFF) when the equilibrium was achieved and the equilibrium concentration (mg. L^{-1}), respectively and R (8.314 J/mol K) and known as the universal gas constant. $\Delta S^{o}ads$ and $\Delta H^{o}ads$ values were determined when plotting (ln Kc vs 1/T)(Fig.6). From intercept ($\Delta S^{o}ads$ n /R) can be calculated and ($-\Delta H^{o}ads$ /R) can be determined.

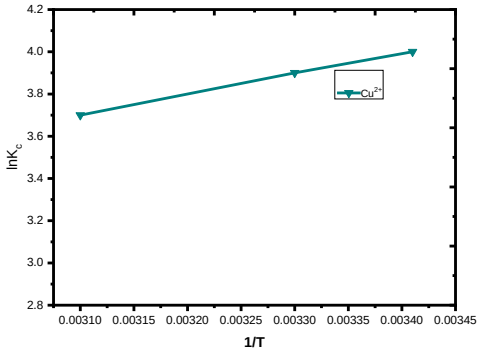


Fig. 6 Effect of temperature on Cu(II) adsorption on OATP-MFF surface

From Table 1 ($\Delta G^{o}ads$) sign value clarifies that metal ion adsorption process by OATP-MFF at room temperature is spontaneous, and negative $\Delta H^{o}ads$ value present that the adsorption process is exothermic in nature in addition to the negative $\Delta S^{o}ads$ values clarifies that as a result of metal ions adsorption onto OATP-MFF system resulting in lowering the randomness and increase the alignment on the surface of modified cellulose. The same behavior was observed by many systems [34].

Table 1: Thermodynamic parameters for the adsorption of single metal cations Cu2+

System	Kc			-$\Delta G^{o}ads$ (KJ/mol)			$\Delta H^{o}ads$ (KJ/mol)	$\Delta S^{o}ads$ (J/mol K)
	293 K	303 K	313 K	293 K	303 K	313 K		
Cu^{2+}.OATP-MFF	268	254	244	13.2	10.2	8.96	-22.65	-33.25

3.4. The effect of time of contact on the metal ion adsorption

The adsorption kinetics of copper metal ion on to OATP-MFF has been elaborated in the range of 30 - 140 minutes as shown in Figure.7.It's observed that the sorption capacity of Cu(II) increases with increasing the time from 30 min to 100 min and become constant after that, it was observed that the sorption capacity of target metal ions become constant at 92 mg/g as sorption capacity.

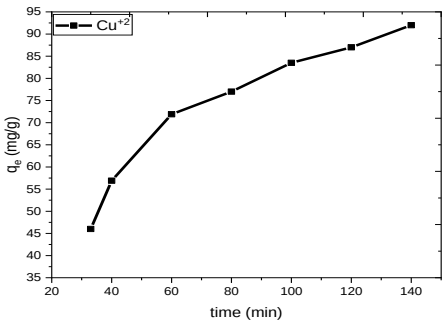


Fig. 7. Effect of contact time on adsorption of Cu(II) on OATP-MFF

Investigation of the kinetic parameters has a great role for sorption system understanding and scheming also important in adsorption rate-determining step estimation. Due to OATP-MFF has many different active functional groups, so that OATP-MFF may provide different interaction types. The first type is present in Eq (6) pseudo-first-order equation and in Eq(7) is the pseudo-second-order equation.

$$\frac{1}{q_{t(ads)}} = \frac{K_1}{q_{e(ads)}} t + \frac{1}{q_{e(ads)}} \quad \text{Eq (6)}$$

$$\frac{1}{q_{t(ads)}} = \frac{1}{q_{e(ads)}} t + \frac{1}{K_2 q_{e^2(ads)}} \quad \text{Eq (7)}$$

Where qe(ads) is the adsorption ability at equilibrium (mg.g-1), qt(ads) is the adsorption ability at a time by minute (mg.g^{-1}), k1 and k2 are sorption rates pseudo 1st and 2nd orders. Table (2) shows the data of the kinetic constants of the studied models.

Table 2: kinetic data of the two studied models for the adsorption of single metal cations Cu^{2+}

Fibers	First-order model		
	k1 (min^{-1})	qe1ads(mg/g)	R2
Cu^{2+}.OATP-MFF	3.2	83.5±3	0.901
Fibers	Second-order model		
	k2 (g/(mg min))	qe2ads (mg/g)	R2
Cu^{2+}.OATP-MFF	3.2 ×10-3	91± 2	0.98

In pseudo 1st and 2nd orders models, sorption rates and equilibrium adsorption ability were estimated and the obtained data close to data in the Table (2) in addition to the value of correlation coefficient which was used for choosing the suitable model. We found that qe well matched with the data of experimental work and R2 correlation coefficient at using pseudo 2nd order closes to unit value so that it is suitable kinetic model for the explanation of the mode of adsorption [35-37].

3.5. Effect of initial concentration of metal ion sorption

The obtained experimental values for both Langmuir and Freundlich isotherm models as tabulated in Table (3). Both of Langmuir equation Eq. (8) and Freundlich equation Eq. (9) are introduced as shown

$$\frac{C_e}{q_e} = \frac{1}{K_1 q_m} + \frac{C_e}{q_m} \quad \text{Eq (8)}$$

$$lnq_e = lnK_f + \frac{1}{n(lnc_e)} \quad \text{Eq (9)}$$

Where, 1/n is the factor of the heterogeneity KF (L/mg) is the constant of Freundlich, Ce (mg/ L) is the target metal ions concentration at equilibrium in aqueous solution and qe (mg/g) is the target metal ion sorption capacity at equilibrium.

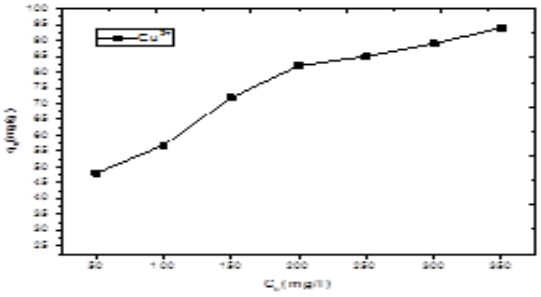


Fig. 8. Effect of metal ion initial concentration on adsorption of Cu(II) on OATP-MFF surface

From the obtained data we can deduce that Langmuir was the most appropriate isotherm model for the experimental data and this model confirms that the adsorption reaction has occurred in monolayer. The adsorption capacity was (92mg/g) ensure that OATP-MFF could be considered as a useful and good chelating agent for copper ions adsorption.

Table 3: experimental data for both Langmuir and Freundlich isotherm models for the adsorption of single metal cations Cu^{2+}

Fibers	Langmuir isotherm constants			
	KL(L/g)	qm(mg/g)	R2	RL
Cu^{2+}. OATP-MFF	18x10-2	92	0.998	(0.014-0.552)

Fibers	Freundlich isotherm constants		
	KF	n	R2
Cu^{2+}. OATP-MFF	11.452	3.1	0.89

3.6. Effect of interfering ions

For studying the selectivity of the provided procedure, many different metal ions were used as interfering ions. The experimental data as shown in (Table. 4) clarify that the studying procedure doesn't affect by different ion concentrations on the determination of the target metal ions. Therefore, it can be deduced the new method has high selectivity to determine the target metal ions in various real samples.

Table 4: Limits of tolerance of interfering ions

Ions	Tolerance limit (mg/l)	% Recovery of Cu^{2+}
Na^{+}	1000	99.6
K^{+}	1000	98.5
Mg^{2+}	500	97.2
Ca^{2+}	500	97.9
Co^{2+}	50	93.6
Ni^{2+}	50	98.1
Al^{3+}	50	97.2
PO_4^{3-}	500	88.9
NO_3^{-}	200	99.1
Succinate	10	98.1
Tatarate	10	91.0
Thiourea	5	77.3
SCN^{-}	5	88.0

3.7. *Sorbent reusability*

The evaluation of sorbent reusability of OATP-MFF material for the adsorption capacity for Cu(II), 3 ml of 0.2 M HNO3 is sufficient for complete elution of metal ions until five cycles with maintaining 95% of its efficiency. The newly synthesized polymer is considered a cheap material and a good sorbent for Cu(II) adsorption.

4. Conclusion

The newly synthesized (OATP-MFF) exhibit high adsorption capacity of 92mg/g this phase was characterized by some techniques for confirmation of its formation. In this work, adsorption was a heat-releasing reaction in nature and was spontaneous at all studied temperatures.This was confirmed from the thermodynamic studies. The Cu^{+2} adsorption kinetics onto OATP-MFF material was quick and well-matched with the pseudo-second-order model and experimental data was well-matched with the Langmuir isotherm model, assuring that the sorption process followed the monolayer copper adsorption and the chemical coordination mechanism.

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