Egypt. J. Chem. **Vol. 64,** No. 7 pp. 3889 - 3901 (2021)

Egyptian Journal of Chemistry

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

Synthesis, Characterization and Analytical Applications of Chemically Modified Cellulose for Remediation of Environmental Pollutants

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Abstract

Carbohydrazides functionalized cellulose (CH-MC) was prepared and characterized using some qualified techniques such as Scanning Electron Microscopy (SEM), Infra-Red (FT-IR), Elemental analysis (EA) and Thermogravimetric analysis (TGA). The prepared CH-MC was employed for uptake of heavy metal ions such as, $Hg^{2+}$and Cu^{2+} from different samples. Sorption parameters: such as pH, temperature, time of sorption and the concentration of sorbent were investigated to determine the best conditions for sorption. The kinetic of sorption agreed with the second-order model and the chemical adsorption is the rate-limiting step. In addition, the sorption isotherm experiments revealed that the best adequate with Langmuir model which the maximum adsorption capacities for $Cu^{2+}$and Hg^{2+} metal ions on CH-MC are 43.3, 64 mg/g, respectively. The real samples including Hg^{2+} and Cu^{2+}were used for analytical applications on the present methodology and the observed data is promising.

Keywords: Adsorption, Carbohydrazide; Cellulose; metal ions, pollutants

1. Introduction

The environmental pollution of heavy metals is one of the big ecological issues It poses a possible danger to humans, plants and animals. Not undergoing biodegradation of the metals. Many of these are water soluble, thus being more available to living systems and accumulating in the environment [1]. Metals, which are significantly toxic to human beings and ecological environments, include chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), manganese (Mn), cadmium (Cd), zinc (Zn), nickel (Ni) and iron (Fe), et [2]. Since Mercury and Copper are widely used for various industrial applications [3], [4] such as mining, metal plating, processing ores, paint and pigments, storage battery industries, tanneries, chloralkaline, boiler production, smelting, alloy and sludge disposal etc. [5]. Mercury bioaccumulation can inactivate important cell functions and Causes a number of diseases including kidney failure, extreme cognitive and movement disorders, hepatic damage, and Minamata [6]. Copper and its compounds are commonly used in many industries, and many possible sources of copper pollution exist. Continued human intake of copper results in necrotic changes in liver and kidney, mucosal irritation, widespread capillary injury, depression, gastrointestinal irritation and lung cancer [5]. Contaminants of wastewater, especially heavy metals, can be removed from wastewater using various well-established techniques. These include adsorption, nanofiltration, reverse osmosis, solvent extraction, chemical precipitation, flotation, coagulation and flocculation, ion exchange, membrane filtration, etc [7-23]. Of all these methods, adsorption has received scientific attention mainly due to its high productivity, low cost, ease of management and high availability among other advantages. Scientists have turned their attention to searching for cheap, readily available biomaterials for wastewater treatment. Some of the well-known natural polymers that are highly concerned with water treatment are chitosan, alginate, lignin, and cellulose [24]. Cellulose is considered the most abundant biopolymer and reusable in nature. The latest trends in using

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Receive Date: 02 March 2021, Revise Date: 24 March 2021, Accept Date: 28 March 2021
DOI: DOI: 10.21608/EJCHEM.2021.65793.3412

biomaterials such as absorption of metals. The original cellulose gives unsatisfactory results that cause chemical and physical changes is required by adding new active group of chelates that allow harmful metal ions to be captured. Modification dependent, for example, on the use of carboxylate and amino groups or amination and sulphonation groups and primary hydroxyl reactions as a chelating group [25]. The periodate of the potassium is known as the selective oxidizing agent that oxidizes two groups of hydroxyls on two adjacent carbon atoms, which is cleared by C_2-C_3 bond in the glucopyranoside ring to form two groups of dialdehyde. [26].

Inspired by those results, the study aimed at the synthesis of N-donor modified cellulose adsorbents, for a selective separation and recovery of Hg (II) and Cu (II) taking into account the coordination chemical characteristics of heavy metals. Carbohydrazide is one of the most useful hydrazine derivatives which have very similar hydrazine properties, are less toxic than hydrazine and are of very interest ligand [27] so it can therefore be used to modify cellulose in the production of new chelating fibres. In this research, carbohydrazide modified cellulose (CH-MC) has been developed and thoroughly studied with different instrumental efficiency. The binding and selectivity studies of the chelating fibres investigated were performed to optimize the various factors influencing adsorption.

2. Experimental

2.1. Reagents and solutions

All the chemicals used in this work, in the purity of the analytical reagent standard, were used as obtained. Sigma-Aldrich, United Kingdom, acquired cellulose powder (C6413 microgranular), carbohydrazide (98 %), potassium periodate (99.8 %), sodium hydroxide (99.99 %). Merck, Darmstadt, Germany, obtained hydrochloric acid (37 percent) and nitric acid (65 per cent). Stock solutions of 250 mg L^{-1} Hg (II) and Cu (II) were prepared by dissolving the required amounts of $HgCl_2$ and $CuSO_4{\cdot}5H_2O$, respectively, in 1 L double distilled water

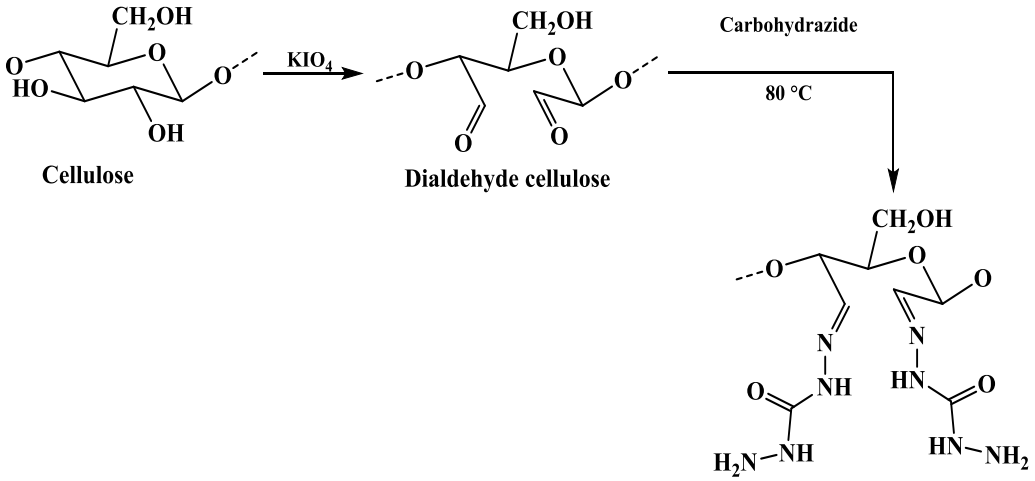
2.2. Synthesis of CH-MC

2.2.1. Preparation of cellulose 2,3-dialdehyde (DAC)

The cellulose powder (500 mg) was suspended in 100 ml ($3g.L^{-1}$) of a freshly prepared potassium periodate solution in a dark brown bottle and the pH was set to pH 5 using acetate buffer. Next, the reactions mixture shook for 2 hours. At approximately 55°C. Then the suspension was filtered and the residual periodate oxidant was removed by dipping the oxidized cellulose into 100 mL 1 percent aqueous solution of ethylene glycol and stirring it up for 30 min. the product was filtrated, washed was absolute ethanol and oven-dried at 50°C Scheme 1 [28].

2.2.2. Preparation of Schiff's bases

In the presence of few drops of triethylamine, oxidized cellulose (500 mg) was refluxed at 80 ° C during 5 h, with 100 ml 1 % w / v alcoholic solution of Carbohydrazide. The white substance collected was purified and thoroughly washed with ethanol. then. double distilled water to remove the excess of carbohydrazide before drying under vacuum at 50 ° C The synthetic-modified cellulose is shown in Scheme 1.



Scheme 1: Synthesis of modified cellulose

2.3. Instrumentation

A Perkin Elmer 2400 CHNS analyzer was used to perform elemental analysis of the native and modified cellulose samples. FT-IR spectra of the analyzed samples were collected using KBr-pressed discs using a Shimadzu 5800 Fourier FT-IR transform spectrometer. Scanning electron microscope (Quanta FEG-250) was used for the morphological surface characterization of the samples. Until SEM analysis, all the samples had been sputter-coated with gold. A newly launched (ICP-OES) (Perkin Elmer Inductively coupled plasma-optical emission spectrometer (Optima 8300, USA).

2.*4. Sorption studies using batch method*

The performance of the synthesized CH-MC polymer for Hg^{2+} and Cu^{2+} recovery and separation were tested in batch experiments.

A 50-ml aliquot was transferred into a 100- ml stoppered bottle containing $Hg^{2+}$and another bottle containing Cu^{2+}. Then, the pH of each solution was adjusted to 6 with 0.1mol L^{-1} HCl and 0.1 mol L^{-1} NaOH) except for the influence of pH studies in which the pH ranged between 1 and 6). After that, The cellulose was added to 0.05 g and the final volume of double distilled water was increased to 50 ml. The mixture was then shaken at a shaking rate of 150 rpm for 2 hours using a thermostatic shaker. At the temperature of 25 ° C. The adsorbent was separated and the remaining metal ions were measured in aqueous solutions. The sorption capacity (mg g−1) of Hg^{2+} and Cu^{2+} by the adsorbent was calculated using equation 1.

$$q_e = (C_o - C_e)\, V/m \qquad \text{Eq. 1}$$

Where the sorption capacity is q_e (mg g−1), the initial concentrations is C_o (mg L^{-1}) and Ce (mg L^{-1}) is metals of metal ions equilibrium concentration in solution. V and m are the volume (ml) and mass (g), respectively, of the solution and are adsorbent.

Metal concentrations in the range of 25-200 mg L^{-1} for 2 h were examined for sorption isothermal. 25 ° C with pH 6. The initial concentration of metal ions was 50 mg L^{-1} to study thermodynamic parameters and the temperature range at pH 6 was between 20-45 ° C.

3. Results and discussion

3.1. Assignment of polymeric samples

3.1.1. Elemental analysis

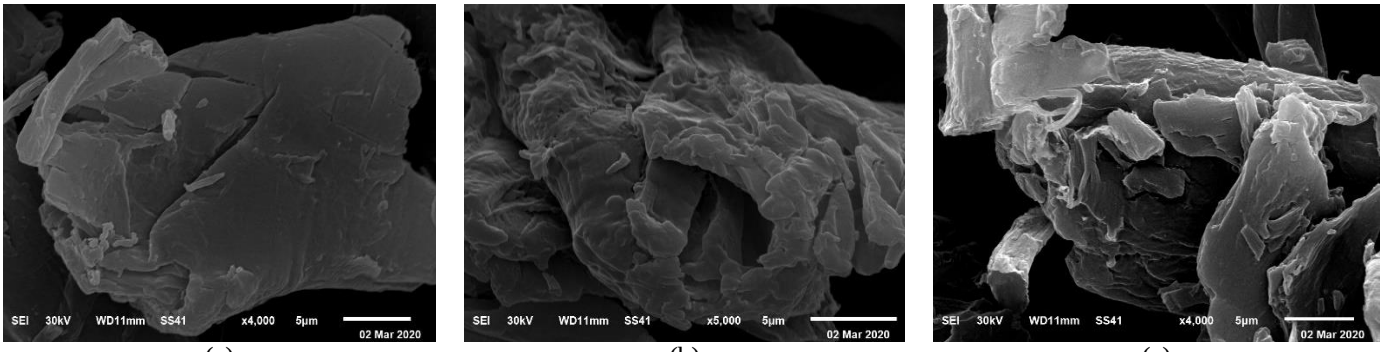
By studying the variance in morphological structure, the results of the elemental analysis of native cellulose, dialdehyde cellulose and carbohydrazide-modified cellulose are Shown in Table 1 Results indicate that the nitrogen content is increased by a good percent after oxidation of cellulose and subsequent condensation with carbohydrazide.

Table 1: Elemental analysis

Fibres	C(%)	H(%)	N(%)
Cellulose	41.55	6.05	--------
dialdehyde-cellulose	40.99	6.02	--------
carbohydrazide-modified cellulose	37.74	5.16	8.18

3.1.2. Scanning electron microscope

Scanning electron microscope (SEM) was used for an analysis of the morphology structures of polymeric samples by oxidized and modified cellulose. As seen on Fig. 1, Rough on the oxidized cellulose surface can be due to time action at oxidation on cellulose powders [25]. The surface roughness in CH-MC can however be due to the chemical reaction of carbohydrazide to oxidized cellulose.



(a) (b) (c)

Fig.1: SEM photos of (a) cellulose powder, (b) oxidized cellulose, (c) carbohydrazide modified cellulose

3.1.3. Infra-red spectra

The following steps were differentiated by FTIR samples for CH-MC synthesis as chelating powder and results were shown in Figure.2. Unmodified cellulose infrared spectra (Fig.2a) showed some peaks at approximately 1070–1150 cm^{-1} were shown by extending C-O's vibrations, 1250–1420 cm^{-1} by bending O-H vibration and 3500–3200 cm−1 by stretching O-H. The dialdehyde cellulose spectrum after periodate oxidation showed an apparent peak of about 1732 cm^{-1}, associated with the newly developed aldehyde stretching vibrations group (Fig. 2b) [29]. After the reaction with carbohydrazide, the spectrum of the prepared CH-MC (Fig. 2c) shows a new peaks at nearly 1660 cm^{-1} and 1550 cm^{-1}, which may be related to stretching vibrations of N=C group and bending vibrations for N-H bond of the Schiff base that formed between the oxidized cellulose dialdehyde groups and the amino group of the carbohydrazide [10, 14]. For better evaluation of the mechanism by which the Hg^{2+} and Cu^{2+} can coordinate with the active carbohydrazide moieties inserted onto the chelating fibers, the FTIR spectra of the Hg^{2+} and Cu^{2+} loaded on CH-MC chelating fibers was carried out and compared to free fibers. As expected the main diagnostic peaks of carbohydrazide moieties showed obvious changes were the shift of bending vibrations for N-H bond from 1550 cm^{-1} to ~1540 $cm^{-1}$for both complexation with Hg^{2+}&Cu^{2+} ions in addition to shift of stretching vibrations of N=C group from 1660 cm^{-1} to ~1650 cm^{-1} as shown in (Fig. 2d,2f)

3.1.4. Thermal studies (Thermogravimetric analysis)

Thermogravimetric analysis (TGA) and the first derivative (DTA) analysis was carried out in the temperature range of 30-800 ºC for the modified cellulose samples to give information about their thermal stability. Thermograms demonstrated that each compound undergoes a series of different degradation steps. TGA of cellulose gives two decomposition steps. On the other hand, thermogram of CH-MC gives four decomposition steps which confirm the modification step of cellulose. The thermal degradation of CH-MC and their complexes with metal ions $Cu^{2+}$and Hg^{2+} were examined under the same state and the total residue were determined as following 18.9, 12.24, 17.47%, respectively. The decreasing in the value of total residues of metal-chelate in case of mercury and copper complexes with comparing to the parent one suggesting that these metal ions show catalytic degradation [14] during their complexation with CH-MC and relatively less stabilization of these metal chelates shown in Figure.3(a, b and c).

3.2. Optimization

3.2.1. Effect of pH

As previously stated, pH significantly influences the chemical adsorption of metal ions from aqueous solutions [14]. In the pH range 1-6 (Fig. 4), the effect of initial pH on the absorption of Hg^{2+} and Cu^{2+} metal ions using CH-MC chelating powder was investigated. It was found that by increasing the pH value, the adsorption of Hg^{2+} and Cu^{2+} metal ions increase. The absorption of metal ions happens by interaction between the modified cellulose's active sites and the metal ions. The majority of active sites with low pH values are protonated so the competitive position between H^{+} and metal ions leads to the decrease in their ability to occupy the metal ions examined.

The extent of adsorption has been studied in accordance with pH and the removal of metal ions at pH=6.0

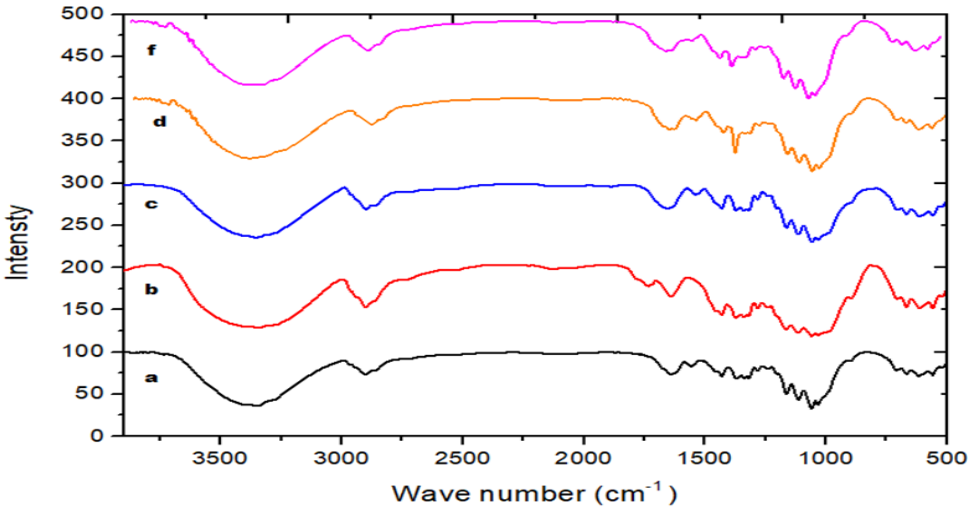


Fig.2: FT-IR spectra of (a) cellulose powder, (b) oxidized cellulose,

(c) carbohydrazide modified cellulose (d) Hg^{2+} CH-MC (f) Cu^{2+} CH-MC

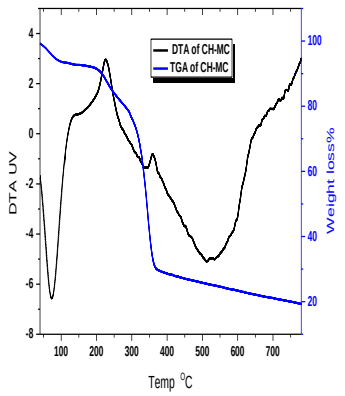


Fig.3a: Thermal analysis of CH-MC. (weight loss as a function of temperature)

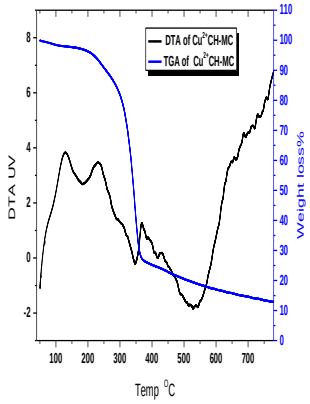


Fig.3b: Thermal analysis of Cu^{2+}CH-MC. (weight loss as a function of temperature)

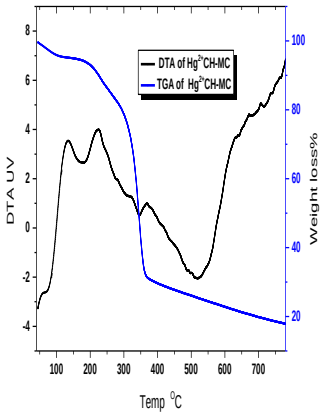


Fig.3c: Thermal analysis of Hg^{2+}TCH-MC. (weight loss as a function of temperature)

Fig. 3: Thermal studies (Thermogravimetric analysis)

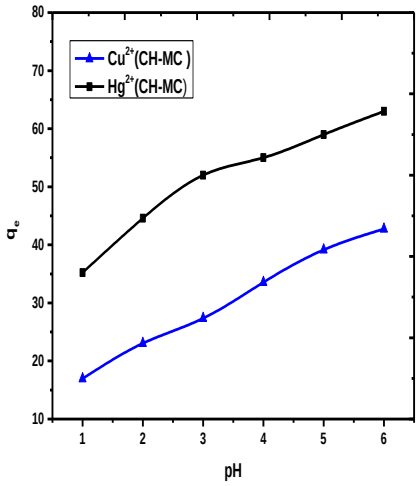


Fig. 4: pH effect on the removal of single metal cations Hg^{2+} and Cu^{2+} (50 ml of 100 mg. L^{-1}) by CH-MC sorbent (0.05 g), with time contact of 4 h, shaking rate 150 rpm, at 25°C.

3.2.2. Temperature effect on the metal ions adsorption

The target metal ion adsorption at different temperatures between 20 and 45°C were calculated by adsorption of the target metal ions at specific Parameters, such as standard free energy (ΔG^o_{ads}), enthalpy heat (ΔH^o_{ads}) and entropy (ΔS^o_{ads}). The constant thermodynamic equilibrium (Kc) was calculated in: thermodynamic parameters

$K_C = C_{ad} / C_e$ Eq (4)

Where C_{ads} is the concentration of metal ions adsorbed at equilibrium on the fibers (mg. g^{-1}), and Ce is the equilibrium concentration (mg. L^{-1}).

$\Delta G^o_{ads} = -RT \ln K_C$ Eq (5)

$\ln KC = (\Delta S^o_{ads} / R) - (\Delta H^o_{ads} / RT)$ Eq (6)

where R is the universal gas constant (8.314 J/mol K). The values of ΔH^o_{ads} and ΔS^o_{ads} were assessed from the slope

$(-\Delta H^o_{ads} /R)$ and the intercept $(\Delta S^o_{ads} /R)$ of the plot of ln Kc vs 1/T

The negative value of ΔG^o_{ads} indicates that the process for adsorption of metal ions by CH-MC is based on the thermodynamic parameters assessed as shown in Table (2). At room temperature, is spontaneous. ΔHoads negative value means that the adsorption process is exothermic in nature and some amount of heat is lost when metal ions are adsorbed. However, due to the adsorption of metal ions to CH-MC, the negative values of some ΔS^o_{ads} indicate the system's lower randomness and higher alignment.[14].

Due to the lower interaction between the metal ions and the active groups in CH-MC, the adsorption capacity of the metal ions decreased by increasing the temperature

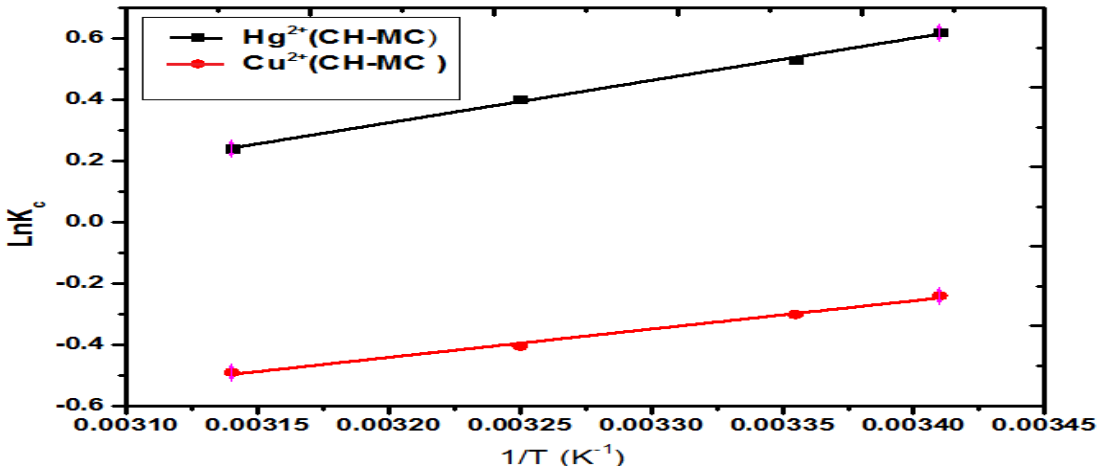


Fig. 5: : Plot of ln KC as a purpose of (1/T) absolute temperature for the adsorption of single metal cations Hg^{2+} and Cu^{2+} on CH-MC

Table 2: Thermodynamic parameters for the adsorption of single metal ions Hg^{2+} and Cu^{2+} on CH-MC.

System	K_c				$-\Delta G^o_{ads}$ (KJ/mol)				ΔH^o_{ads} (KJ/mol)	ΔS^o_{ads} (J/mol K)
	293 K	298 K	308 K	318 K	293 K	298 K	308 K	318 K		
Hg^{2+}(CH-MC)	1.857	1.7	1.5	1.27	1.508	1.131	1.024	0.635	- 11.476	-34.00
Cu^{2+}(CH-MC)	0.786	0.739	0.666	0.612	0.587	0.749	1.040	1.298	-7.695	-28.26

3.2.3. Effect of contact time on metal ions adsorption

The effect of contact time on the adsorption of the metal ions studied by CH-MC was investigated within 15-240 minutes. Figure. 5 shows that the metal ions have an increased adsorption capacity of 15-120 minutes over time and that the removal of the individual metal cations Hg^{2+} and Cu^{2+}remains constant. Thus, 120 min was selected as the optimal time for further experiments.

The study of kinetic parameters has an important rule for the arrangement of sorption systems, better understanding of the mechanism for sorption and the determination of the adsorptive rate. Due to the existence of several active functional groups in CH-MC, CH-MC may show different interaction types. The first type is equation of the pseudo-first order, as shown in Eq. (7) and an equation of the pseudo-second order as shown in Eq. (8)

$$1/q_t(ads) = k_1/ q_{e(ads)}t + 1/q_{e(ads)} \quad \text{Eq.(7)}$$

$$t/q_t(ads)=1/k_2q_e^{2}{}_{(ads)}+(1/q_{e(ads)})t \quad \text{Eq.(8)}$$

Where the adsorption capacity at equilibrium and t time is $q_{e(ads)}$ (mg. g^{-1}), and the adsorption capacity at t time (min) is $q_{t(ads)}$. K_2 is the pseudo-second-order adsorption rate constant and K_1 is pseudo-first-order sorption rate constant.

The K and $q_{e(ads)}$ for the two models were often computed together, and for testing the kinétic model that fits the testing, a model which closes the experimental adsorption data and the correlation coefficient was used. Table 3 Returns the kinetic parameters for the existing models. Using pseudo-second-order kinetic models, the experimental values $q_{e(ads)}$ match the calculated values, even depending on the coefficients of correlation (R^2) achieved. The pseudo-second - order equation is therefore appropriate for experimental kinetic data. Many previous sorption studies have been able to fit the model of the second order [14].

3.2.4. Effect of initial concentration of the investigated metal ions

Studies of adsorption isotherm are essential in explaining the interaction between the metal ions and the chelating CH-MC

a) Freundlich $\ln q_e= \ln K_F+1/n (\ln C_e)$

Are the most used versions of isotherms. where C_e and q_e are respectively the concentration of the adsorbate cation at equilibrium in the liquid phase and q_e is the corresponding concentration of the adsorbate in the solid phase, K_f and n being Freundlich coefficients,

b) Langmuir. $C_e /q_e = ((1/(K_l q_m))+(C_e /q_m)$

where K_l and q_m are Langmuir coefficients representing the equilibrium constant for the

adsorbate-–adsorbent equilibrium and the monolayer capacity, respectively.

The linear Freundlich and Langmuir plots are obtained by plotting (i) ln q_e vs. ln C_e and (ii) C_e/q_e vs. C_e, respectively, from which the adsorption coefficients could be evaluated [30].

At 25ºC and an initial ion concentration of 25 to 200 mg/Lwere developed with the adsorption isothermal experiments (Figure 6). For the Langmuir and Freundlich isothermal model, the experimental data collected were used and all parameters were presented in Table 4. The correlation coefficient value shows that Langmuir is better suited for experimental results in adsorption. The Langmuir isotherm model shows that the adsorption of metal ions is monolayer, as assumed, occurred on an adsorbent surface and was primarily chemical adsorption. The maximum adsorption capacities for $Cu^{2+}$and Hg^{2+} metal ions with CH-MC are 43.3, 64 mg/g, respectively. Target metal ions' high adsorption capacities show that CH-MC chelating fibers are excellent adsorbents that can be used effectively to treat wastewater samples.

Table 4 provides a comparison of the proposed modified adsorbent with the other adsorbents.

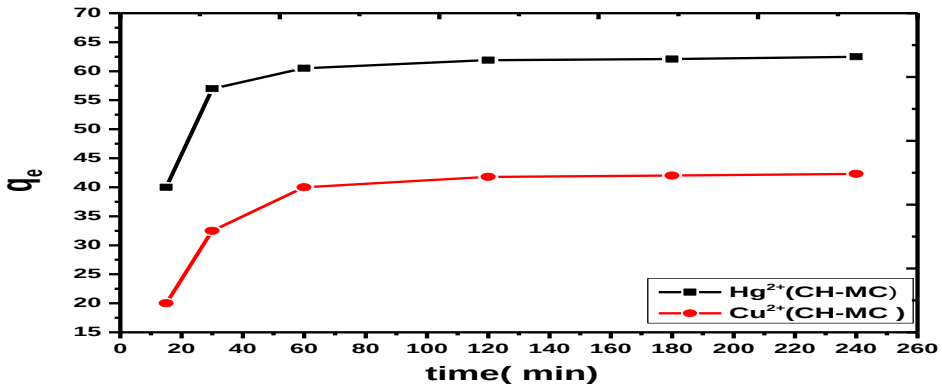


Fig.6. Influence of time contact on the removal of single metal cations Hg^{2+} (50 ml of 100 mg. L^{-1}), by CH-MC. sorbent (0,05 g), pH 6, rate of shaking 150 rpm, at 25ºC.

Table 3: Kinetic parameters for the adsorption of Hg^{2+} and $Cu^{2+}$by CH-MC.

Fibres	First-order model		
	k_1 (min^{-1})	q_{e1ads}(mg/g)	R^2
Cu^{2+}. CH-MC	20.9	49.8	0.942
Hg^{2+}. CH-MC	9.45	67.79	0.886

Fibres	Second-order model		
	k_2 (g/(mg min))	q_{e2ads} (mg/g)	R^2
Cu^{2+}.CH-MC	1.817×10^{-3}	44.9	0.997
Hg^{2+}. TCH -MC	2.85×10^{-3}	64.18	0.999

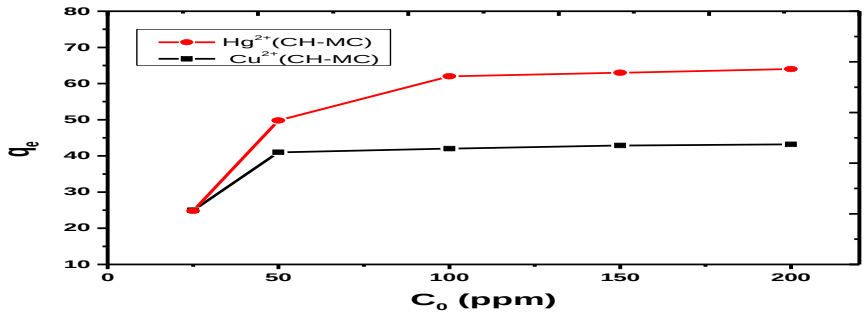


Fig.7: Adsorption isotherms of single metal cations Hg^{2+} and Cu^{2+} by CH-MC (50ml of (25-200) mg/L) initial concentrations, by CH-MC sorbent (0.050 g), with pH 6, rate of shaking 150 rpm, at 25 ºC.

Table 4: Physicochemical adsorption of metal ions Hg^{2+} by CH-MC chelating fibres.

Fibers	Langmuir isotherm constants		
	K_L(L/g)	q_m(mg/g)	R^2
Cu^{2+}. CH -MC	1.53	43.34	0.999
Hg^{2+}.CH-MC	1.81	63.97	0.999
Fibers	Freundlich isotherm constants		
	K_F	n	R^2
Cu^{2+}. CH -MC	32.72	16.07	0.937
Hg^{2+}. CH -MC	41.05	10.37	0.498

3.2.5. Desorption study

Several methods of eluting reagents were investigated with the recovery of adsorbed elements as shown in (**Table** 5), and 3 mL 0.2 mol / L HNO3 solution was the best eluting form to be found, enough to provide full elution of the metal ions with recovery > 95%.

Table 5: Percent recovery for Cu^{2+} and Hg^{2+} with the eluting solution

Eluting solution	Recovery, (%)	
	Cu^{2+}	Hg^{2+}
0.1 mol / L HNO_3	87.5	82.2
0.15 mol/L HNO3	93.7	91.9
0.2 mol/L HNO3	99.6	97.9

3.2.6. Sorbent reusability

Five adsorption-desorption cycles had been performed under the optimum conditions to assess the reusability of CH-MC and the results were presented in Table 6. the modified cellulose adsorption efficiency did not show a significant decrease. After the fifth cycle, fibers retain approximately 95 per cent of their original capacity. Therefore, CH-MC may be a promising adsorbent for removing $Cu^{2+}$and Hg^{2+} metal ions from wastewater

Table 6: Repeated adsorption of metal ions Cu^{2+} and Hg^{2+} (50 ml of 50 mg L^{-1}) by CH-MC sorbent (0.050 g), pH 6, time of shaking 120 min, 25ºC, desorption by 3 mL of 0.2 mol/L HNO_3

Cycle number	Recovery (%)	
	Cu^{2+}	Hg^{2+}
1	99.8	99.3
2	98.4	98.5
3	97.3	97.2
4	96.5	96.5
5	95.4	94.8

3.2.7. Effect of interfering ions

In order to test the selectivity of a given method, the effects of different ions on the 100 µg/ ml determination of the metal ions studied were measured under optimized conditions. The test results (Table 7) explain that the metal ions tested in the optimum working conditions defined in the procedure are not obviously affected. It can therefore be deducted that the method proposed has an excellent selectiveness in determining the metal ions measured in different actual samples, which indicates that the procedure proposed is very selective in determining the metal ions studied in different real samples

3.2.8. Applications

The CH-MC sorbent suggested was used for the separation and recovery of $Cu^{2+}$and Hg^{2+} ions. from different real samples, Surface water samples were collected from (Bohia intake of Sinbellawien water station), Tap water was collected from EL-Mansoura city and Ground water was collected from Belbeis Desert. These true samples also received several amounts of Hg (II). ICP-OES determined the concentrations of $Cu^{2+}$and Hg^{2+} following the desorption process. Furthermore, a good agreement between the added and measured analyte quantities reveals that CH-MC sorbent could efficiently be employed with high accuracy and precision to select and determine $Cu^{2+}$and Hg^{2+} ions in real samples. The results showed in Table 8 that the CH-MC sorbent was valid for the recovery of $Cu^{2+}$and Hg^{2+}.

3.2.9. Comparison of the proposed adsorbent with other cited adsorbents

A comparison between the performance of the present adsorbent and other adsorbents previously reported in the literature is presented in Table 9. When comparing different adsorbents for the separation of PMs, the sorption capacity and the type of sample matrices on which the separation is performed should be taken into consideration. As shown in Table 9, the present adsorbent has relatively high capacities for the recovery of Hg^{2+} and Cu^{2+} ions compared to other adsorbents.

4. Conclusions

The new carbohydrazide-modified cellulose chelating fibers (CH-MC) are prepared and characterized by different instrumental techniques. Thermodynamic studies have shown that the adsorption in nature is exothermic and spontaneous at all temperatures. The kinetics of adsorption of metal ions in the CH-MC sorbent were rapid and formed in the second-order pseudo model, confirming the mechanical mechanism of chemical coordination. The model of Langmuir isotherm has also been well matched with the experimental data and confirms the adsorption in metal ion monolayers.

Table 7: Limits of tolerance of interfering ions

Ions	Tolerance limit (mg/l)	% Recovery	
		Cu^{2+}	Hg^{2+}
Na^{+}	1000	99.0	97.3
K^{+}	1000	98.1	97.8
Mg^{2+}	500	97.8	98.2
Ca^{2+}	500	97.8	99.0
Co^{2+}	50	97.2	99.0
Ni^{2+}	50	98.0	98.6
Al^{3+}	50	97.5	95.7
PO_4^{3-}	500	99.0	99.0
Acetate	50	97.5	97.8
Oxalate	50	98.6	98.4
Citrate	50	96.8	98.7
NO_3^{-}	200	99.2	99.9
Cl^{-}	1000	98.6	98.7
HCO_3^{-}	1000	97.5	98.0
SO_4^{2-}	1000	99.2	99.7
Succinate	30	98.8	97.8
Tatarate	30	91.9	89.6
Thiourea	50	73.2	69.2
Ascorbate	100	96.2	97.1
SCN^{-}	10	79.9	83.6

Table 8. Analysis of $Cu^{2+}$and Hg^{2+} ions in water samples after separation and recovery by CH-MC sorbent

Water sample	Metal ions	Added ($\mu g\ mL^{-1}$)	Found ($\mu g\ mL^{-1}$)	Recovery (%)	RSD (%)
Tap water	Hg^{2+}	5	4.843	96.8	1.1
	Cu^{2+}	5	4.78	95.6	1.6
Ground water	Hg^{2+}	5	4.74	94.8	1.3
	Cu^{2+}	5	4.802	96.04	1.2
Surface water	Hg^{2+}	5	4.765	95.3	1.2
	Cu^{2+}	5	4.806	96.12	1.3

Table 9: Comparison of maximum sorption capacity of Hg^{2+} and Cu by proposed method with newly published method

Ions	Adsorbent	q_e (adsorption capacity) mg/g	pH	References
Hg^{2+}, Cu^{2+}	expanded perlite	0.35,1.95	6.5	[31]
Cu^{2+}	Cationic wheat straw	33.4	4-4.5	[32]
Hg^{2+}, Cu^{2+}	A chitosan–thioglyceraldehyde Schiff's base cross-linked magnetic resin (CSTG)	(98 ± 2, 76 ± 1)	5.0	[33]
Hg^{2+}, Cu^{2+}	rice straw	(22.05, 8.128)	5.0	[34]
Hg^{2+}	Magnetic nanoparticles doped with 1,5-diphenylcarbazide	44	<6	[35]
Hg^{2+}	Silica gel modified with 2-(2-oxoethyl)hydrazine carbothioamide	37.5	3	[36]
Hg^{2+}, Cu^{2+}	resins based on poly (methylmethacrylate-co-maleic anhydride)	63, 71.14	3 and 9	[37]
Cu^{2+}	PVA/p(NIPAm-AAc) core-shell nanogels adsorbent	94	6	[12]

Cu^{2+}	barley straws	4.64	6	[5]
Cu^{2+}	clinoptilolite	25.76	7.5	[38]
Hg^{2+}	thiol wheat straw	72.46	4-7	[39]
Hg^{2+}	Rhodamine hydrazide modifying Fe_3O_4 microspheres	7.5	-	[40]
Hg^{2+},	carbohydrazide-modified cellulose	**64**	6	Present work
Cu2+	carbohydrazide-modified cellulose	**43**	6	Present work

4. Conclusion

CMSD chelating fibers were synthesized and identified by efficient techniques. Additionally, the polymeric material CMSD was used in batch method to assess the optimal situations which affects the Hg^{2+} sorption. Regarding the thermodynamic parameters, the sorption processes were exothermic and spontaneous at various temperatures. The kinetics studies of Hg^{2+} metal ions onto CMSD. The adsorption load of modified sawdust for Hg(II) was markedly improved because of the introduction of carboxylic groups on CMSD surface throughout the modification, and it had a linear dependence on carboxylic sites level to some extent.

5. Conflicts of interest

"There are no conflicts to declare".

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