



Synthesis and Application of Carbohydrazides Modified Cellulose for Selective Separation of Hg²⁺ from different municipality Samples

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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). The prepared CH-MC was employed for uptake of heavy metal ions such as, Hg²⁺ from different samples. Sorption parameters: such as time of sorption, pH, temperature 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 sorption uptake of (CH-MC) were 64 mg. g⁻¹ for Hg²⁺. The real samples including Hg²⁺ were used for analytical applications on the present methodology and the observed data is promising.

keywords: Carbohydrazides functionalized cellulose (CH-MC). Carbohydrazides ; Removal of metal cations

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 is widely used For various industrial applications [3] such as mining, metal plating, processing ores, paint and pigments, storage battery industries, tanneries, chloralkali , boiler production, smelting, alloy and sludge disposal etc.[4].

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 [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 [6] . 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 [7].

Cellulose is considered the most abundant biopolymer and reusable in nature. The latest trends in using biomaterials such as absorption of metals. As a metal scraper, 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 groups of amination and sulphonation, and primary hydroxyl reactions as accelerating groups [8].

The periodate of the potassium is known as the selective oxidizing agent that oxidizes two groups of hydroxyl on two adjacent carbon atoms, which is cleared by C2-C3 bond in the glucopyranoid ring to form two groups of dialdehyde. [9].

Inspired by those results, The study aimed at the synthesis and selective separation and recovery of N-donor modified cellulosic adsorbents for Hg (II) taking into account the coordination of heavy metal chemicals. 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 [10] 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. To optimize the various factors influencing the adsorption, binding and selectivity studies of the chelating fibers were performed.

2. Experimental and methods

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 %), sodium hydroxide (99.99 %) potassium periodate (99.8 %), Merck, Darmstadt, Germany, obtained nitric acid (65 per cent) and hydrochloric acid (37 percent) .250 mg L⁻¹ Hg(II) stock solutions were prepared by dissolving the necessary amounts of HgCl₂ in 1 L of double distilled water.

2.2. Synthesis of CH-MC

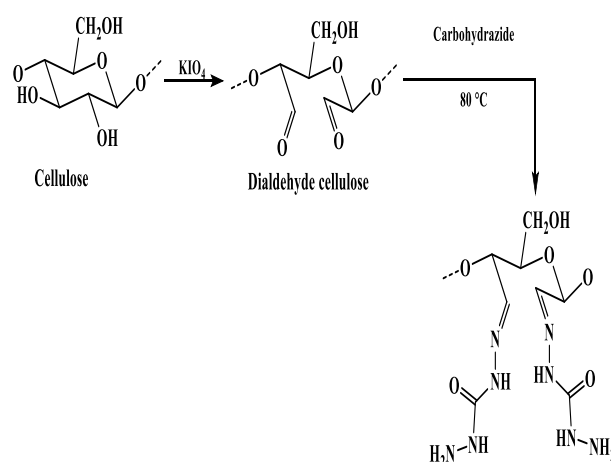
2.2.1. Preparation of cellulose 2,3-dialdehyde (DAC)

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 the aqueous solution of ethylene glycol 100 mL 1

percent and stirring it up for 30 minute. the product was filtrated, washed was absolute ethanol and oven-dried at 50°C Scheme 1 [11].

2.2.2. Preparation of Schiff's bases

By adding 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. Characterization of samples

A Perkin Elmer 2400 CHNS analyzer was used to perform elemental analysis of the modified and native cellulose samples. FT-IR spectra of the analysed samples were collected using KBr-pressed discs using a Shimadzu 5800 Fourier FT-IR transform spectrometer. Scanning electron microscope (Quanta FEG-250) . A newly launched (ICP-OES) (Perkin Elmer Inductively coupled plasma-optical emission spectrometer (Optima 8300, USA).

2.4. batch method used for Sorption studies

The performance of the synthesized CH-MC polymer for Hg (II) separation and recovery was tested in batch experiments.

A 50-ml aliquot was transferred into a 100-ml stoppered bottle containing Hg (II). Then, the pH of each solution was adjusted to 6 with HCl and 1⁻ mol L⁻¹ 0.1⁻ mol L⁻¹ NaOH (except for the impact of pH studies in which the pH scale 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 150 rpm for 2 hours shaking rate using a thermostatic shaker. At the temperature of 25 ° C. separated of the adsorbent and the remaining metal ions were measured in aqueous solutions. Equation 1 was applied to measure the sorption capacity by the adsorbent of Hg(II) (mg g^{-1}).

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

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

Metal concentrations in the scale of 25-200 mg L^{-1} for 2 h were examined for sorption isothermic. 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. observations and discussion.

3.1. Polymer sample characterization

3.1.1. Elemental analysis

Elemental analysis results of native cellulose, dialdehyde cellulose and carbonyl-oxidized 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 carbonyl-oxidized cellulose.

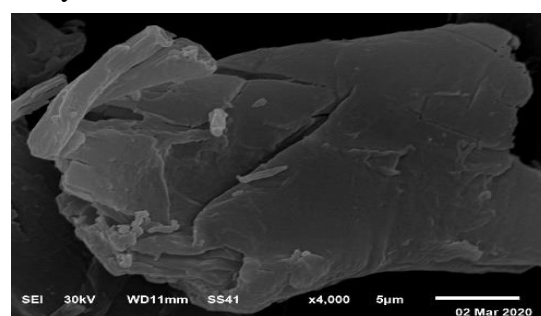
Table 1: Elemental analysis

Fibers	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Cellulose	41.55	6.05	-----
dialdehyde-cellulose	40.99	6.02	-----
carbonyl-oxidized cellulose	37.74	5.16	8.18

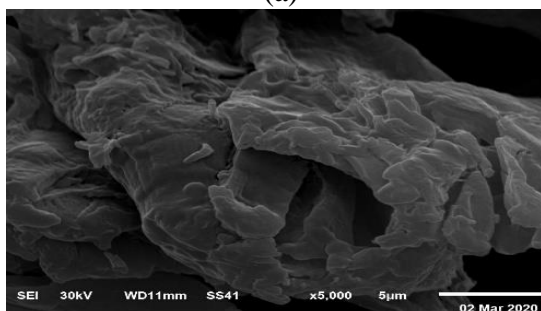
3.1.2. Scanning electron microscope

Scanning electron microscope (SEM) was used for an analysis of the morphology structures of polymeric samples by modified cellulose and oxidized. As seen on Fig. 1, Rough on the oxidized cellulose surface can be due to time action at oxidation on cellulose

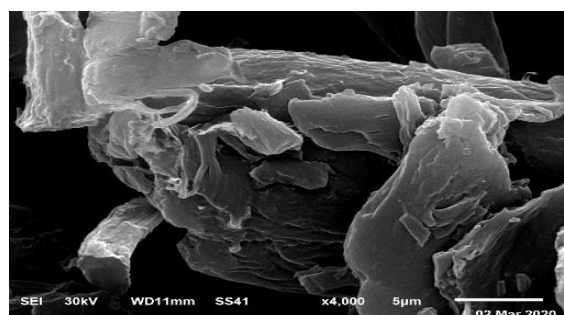
powders[8]. The surface roughness in CH-MC can however be due to the chemical reaction of carbonyl-oxidized cellulose.



(a)



(b)



(c)

Fig.1: SEM photos of (a) powdered cellulose (b) oxidized cellulose, (c) carbonyl-oxidized cellulose

3.1.3. Spectrum infrared

The following passes 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 3200-3500 cm^{-1} by stretching O-H. The dialdehyde cellulose range of spectrum after periodate oxidation shown an apparent peak of around 1732 cm^{-1} , associated with the newly developed aldehyde stretching vibrations group (Fig. 2b)[12]. After the reactions with carbonyl-oxidized cellulose, A new peak of almost 1660 cm^{-1} and 1550 cm^{-1} shows the spectrum of the CH-MC (Fig. 2c).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 carbohydrazone [13-14]. To better assess the mechanism through which the Hg^{2+} can be coordinated with the active carbohydrazone motives in the chelating fibres, The Hg^{2+} loaded CH-MC chelating fibers have been made up of the FTIR spectrum and compared to free Hg^{2+} . The main diagnostic peaks of the carbohydrazone moieties showed apparent modifications when the Hg^{2+} ions were complexed and these changes were the shift of bending vibrations for N-H bond from 1550 cm^{-1} to 1540 cm^{-1} in addition to shift of stretching vibrations of N=C group from 1660 cm^{-1} to 1650 cm^{-1} as shown in (Fig. 2d)

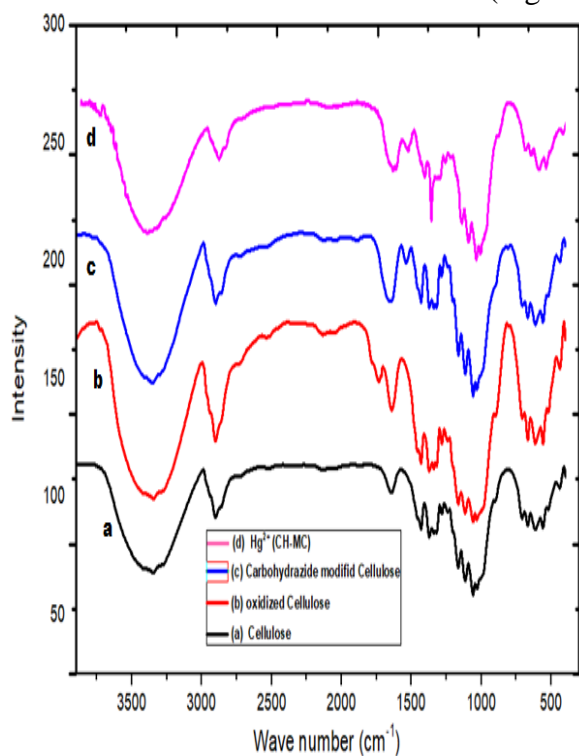


Fig.2: FT-IR spectra of (a) cellulose powder, (b) oxidized cellulose, (c) carbohydrazone modified cellulose (d) Hg^{2+} CH-MC

3.2. Optimization

3.2.1. Effect of pH

As previously stated, pH significantly influences The chemical adsorption from aqueous solutions of metal ions [14]. In the pH range 1-6 (Fig. 3), the effect of initial pH on the absorption of Hg^{2+} metal ions using CH-MC chelating powder was investigated. It was found that by increasing the pH value, the adsorption of Hg^{2+} metal ions increase. The

absorption of metal ions happens by interaction between the modified cellulose's active sites and ions of metal. The major part of active sites with a low pH are protonated in order to reduce their ability to hold the metal ions examined by the competition between H^+ and metal ions..

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

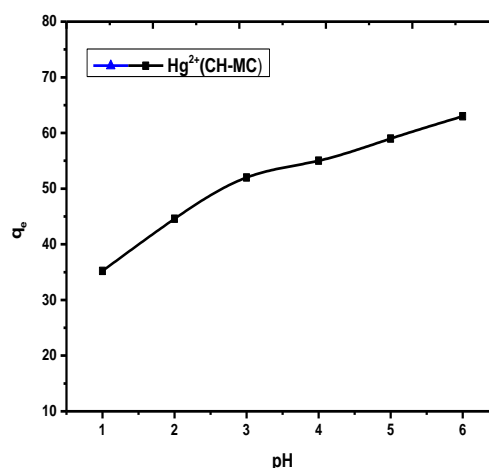


Fig. 3: pH effort for the removal, from CH-MC Sorbent (0.05 g), with 4 hour contact times, with 150 rpm shaking speed, at $25^{\circ}C$, of the single metal cations, Hg^{2+} and Cu^{2+} (50 ml of 100 mg L^{-1})

3.2.2. Temperature effects on the adsorption of metal ions

The target metal ion adsorption at different temperatures between 20 and $45^{\circ}C$ were calculated by target metal ion adsorption at specific Parameters, such as standard free energy (ΔG°_{ads}), enthalpy heat (ΔH°_{ads}) and Hg^{2+} metal adsorption entropy (ΔS°_{ads}). The constant thermodynamic equilibrium (K_c) was calculated in: thermodynamic parameters

$$K_c = C_{ad} / C_e \quad \text{Eq (4)}$$

When C_{ads} is the concentration on the fibers of metal ions sorbed in equilibrium (mg. g-1), and C_e is the concentration of equilibrium (mg. L-1).

$$\Delta G^{\circ}_{ads} = -RT \ln K_c \quad \text{Eq (5)}$$

$$\ln K_c = (\Delta S^{\circ}_{ads} / R) - (\Delta H^{\circ}_{ads} / RT) \quad \text{Eq (6)}$$

Where the universal gas (8.314 J / mol K) consistent is R .

The values ΔH°_{ads} and ΔS°_{ads} were evaluated from the slope.

$(-\Delta H_{\text{ads}}^{\circ} / R)$ and intercept $((\Delta S_{\text{ads}}^{\circ} / R))$ of the plot of $\ln K_c$ vs $1/T$.

The (-ve) value of $\Delta G_{\text{ads}}^{\circ}$ Indicates that the CH-MC adsorption process is based upon the thermodynamic parameters evaluated as shown in Table (2). At room temperature, is spontaneous. $\Delta H_{\text{ads}}^{\circ}$ negative value means that the process of adsorption is exothermic and

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

System	K_c				$-\Delta G_{\text{ads}}^{\circ}$ (KJ/mol)				$\Delta H_{\text{ads}}^{\circ}$ (KJ/mol)	$\Delta S_{\text{ads}}^{\circ}$ (J/mol K)
	293 K	298 K	308 K	318 K	293 K	298 K	308 K	318 K		
Hg^{2+} (C H-MC)	1.857	1.7	1.5	1.27	1.508	1.131	1.024	0.635	- 11.476	-34.00

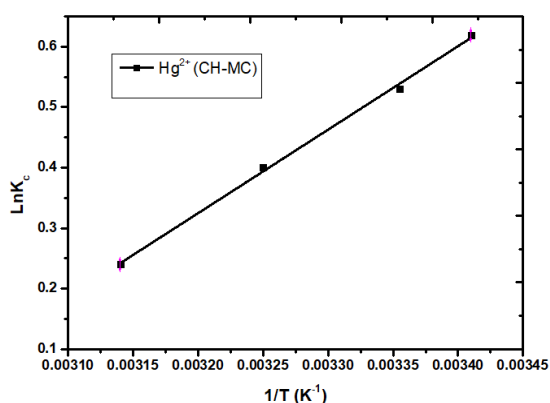


Fig. 4: Plot of $\ln K_c$ to $(1 / T)$ absolute temperature on CH-MC for single metal cations Hg^{2+} adsorption.

3.2.3. Contact time effect on adsorption of metal ions

In 15-240 minutes, The impact of contact time was investigated for CH-MC adsorption of metal ions.. 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+} remains constant. Thus, 120 minute was selected as The optimal experimental time.

Kinetic parameters are a key principle to be studied in order to organize sorption systems, to better understand the sorption mechanism and

to measure an adsorption rate. Because there are several active functional groups in CH-MC, various types of interactions can occur. The first is a pseudo-first order equation, as shown in Eq. (7) and the pseudo-second - order equation as described in the eq. (8)

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

$$t/q_t(\text{ads}) = 1/k_2q_{\text{e}(\text{ads})}^2 + (1/q_{\text{e}(\text{ads})}) t \quad \text{Eq.(8)}$$

some heat is lost when metal ions are adsorbed. However, due to the adsorption of metal ions to CH-MC, the negative values of some $\Delta S_{\text{ads}}^{\circ}$ indicate the system's lower randomness and higher alignment.[14]. As the metal ions and active groups in CH-MC interact lower, the adsorption capacity of the metal ions decreased as the temperature increased.

Where the adsorption capacity at equilibrium and t time is $q_{\text{e}(\text{ads})}$ (mg. g-1), and

the adsorption capacity at t time (min) is $q_t(\text{ads})$. K_2 is the constant pseudo-second order adsorption rate, and K_1 is the constant pseudo-first order sorption rate.

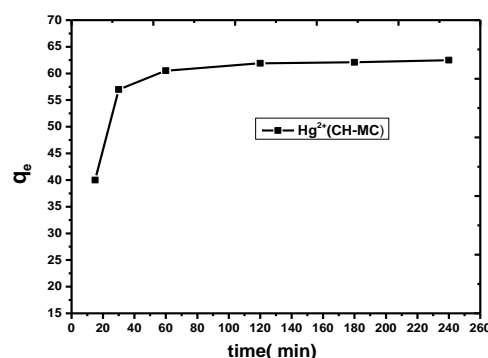


Fig.5. Time contact influence on individual Hg^{2+} metal cations removed (50 ml of 100 mg. L-1) by CH-MC. Sorbed (0,05 g), pH-6, 150 rpm rhythm, 25°C .

The K and $q_{\text{e}(\text{ads})}$ for the two models were often computed together, and for testing the kinetic model that fits the testing, A model was used to close experimental data on adsorption and the correlation coefficient. **Table 3** Returns the kinetic parameters for the existing models. Using kinetic models of pseudo second order, the experimental values $q_{\text{e}(\text{ads})}$ match the calculated values, even depending on the coefficients of correlation (R^2) achieved. Thus, the pseudo-second order equation is suitable for experimental kinetic data. Many past sorption studies were able to fit the second order model [15].

Table 3: Kinetic parameters for the

Fibers model of First-order			
k_1 (min ⁻¹)	q_{e1ads} (mg/g)	R^2	
Hg ²⁺ . CH-MC	9.45	67.79	0.886
Fibers model of Second-order			
k_2 (g/(mg min))	q_{e2ads} (mg/g)	R^2	
Hg ²⁺ . CH -MC	2.85×10^{-3}	64.18	0.999

adsorption of Hg²⁺ by CH-MC.3.2.4. Initial concentration effect of the metal ions investigated

The interaction between the metal ions and chelating CH-MC is important for the study of isotherm of adsorption

a) Freundlich $\ln q_e = \ln K_F + 1/n (\ln C_e)$ (Eq.9)

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. $C_e / q_e = (1/(K_L q_m)) + (C_e / q_m)$ (Eq.10)

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[16].

At 25°C and an initial ion concentration of 25 to 200 mg l⁻¹ were 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 value coefficient 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. For Hg²⁺ + CH-MC metal ions, the maximum adsorption capacity is 64 mg / g. The high capacity of the target metal ions for adsorbing CH-MC chelating fibers demonstrates that they are excellent adsorbents

for efficient treatment of the waste water samples

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

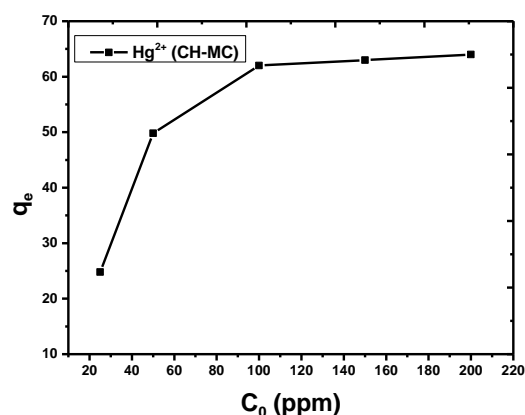


Fig.6: Adsorption isotherms of single metal cations Hg²⁺ CH-MC (50ml of (25-200) mg/L) initial concentrations, by CH-MC sorbent (0.050 g), with pH 6, rate of shaking 150 rpm, at 25 °C.

Table 4: CH-MC Chelating Fibers are physicochemical adsorption of metal ions Hg²⁺

Fibers constants of Langmuir isotherm constants			
K_L (L/g)	q_m (mg/g)	R^2	
Hg ²⁺ .CH-MC	1.81	63.97	0.999
Fibers Freundlich isotherm constants			
K_F	n	R^2	
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 recovery > 95 percent of the metal ions.

3.2.6. Sorbent reusability

Five adsorption-desorption cycles had been performed under the optimum conditions to assess the reusability of CH-MC and Table 6 showed the results. There was no significant decrease in the modified cellulose adsorption efficiency. Fibers retain about 95% of their original capacity following the fifth cycle. Therefore, CH-MC may be a promising adsorbent for removing Hg²⁺ metal ions from wastewater

Table 4. Analysis of Hg(II) ions water in samples by after separation and recovery CH-MC sorbent

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

Table 5: Percent recovery for Hg with the eluting solution

Eluting solution/ mol / LHNO ₃	Recovery, (%)
	Hg ²⁺
0.1	82.2
0.15	91.9
0.2	97.9

Table 6: Repetitive adsorption by CH-MC (0,050 g), pH 6, shaking times 120 min, 25°C, desorption by 3mL of 0,2 mol / L HNO₃ of Hg²⁺ metal ions (50 ml of 50 mg L⁻¹).

Cycle number	Recovery (%)
	Hg ²⁺
1	99.3
2	98.5
3	97.2
4	96.5
5	94.8

Table 7: Tolerance limits of the interfering ions

Ions	Tolerance limit (mg/l)	% Recovery
		Hg ²⁺
Na ⁺	1000	97.3
K ⁺	1000	97.8
Mg ²⁺	500	98.2
Ca ²⁺	500	99.0
Co ²⁺	50	99.0
Ni ²⁺	50	98.6
Al ³⁺	50	95.7
PO ₄ ³⁻	500	99.0
Acetate	50	97.8
Oxalate	50	98.4
Citrate	50	99.7
NO ₃ ⁻	200	99.9
Cl ⁻	1000	98.7
HCO ₃ ⁻	1000	98.0
SO ₄ ²⁻	1000	99.7
Succinate	30	97.8
Tartrate	30	89.6
Thiourea	50	69.2
Ascorbate	100	97.1
SCN ⁻	10	83.6

3.2.7. Effect of ion interference

The effects of different ions were measured under optimized conditions in order to test the selectivity of the given method for 100 $\mu\text{g} / \text{ml}$ metal ion measurement. The result of tests (see Table 7) shows that the tested metal ions are not clearly affected under the optimum working

conditions defined in the procedure. It can therefore be deduced 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 Hg(II) 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 Hg(II) 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 Hg(II) ions in real samples. The results showed in Table 4 that the CH-MC sorbent was valide for the recovery of Hg(II)

3.2.9. Comparison of the adsorbent proposed with other adsorbents referred to

Table 9 presents a comparison of the performance of the current adsorbent with the previously reported adsorbents in the literature. The sorption capacity and type of sample matrices on which the separation is performed should be taken into consideration in comparing different adsorbents for the separation of PMs. The current adsorber has relatively high regeneration capacity of Hg(II) ions, as shown in Table 9, compared to other adsorbents.

4. Conclusions

New cellulose chelating fibers (CH-MC) modified by carbohydrazide are developed and characterized by different instruments. Studies of thermodynamic indicate that adsorption in

nature at all temperatures is exothermic and spontaneous. In the CH-MC sorbent, the kinetics of metal adsorption were quick and in the second-order pseudo model formed, which confirm the mechanism of mechanical chemical

coordination. The Langmuir isotherm model also matches the experimental data well and confirms the adsorption in metal ion monolayers..

Table 9: Comparison of maximum sorption capacity of Hg²⁺ by proposed method with newly published method

Ions	Adsorbent	q _e (adsorption capacity) mg/g	pH	References
Hg ²⁺ ,	expanded perlite	0.35	6.5	[17]
Hg ²⁺ ,	A chitosan–thioglyceraldehyde Schiff's base cross-linked magnetic resin (CSTG)	(98 ± 2)	5.0	[18]
Hg ²⁺	rice straw	(22.05)	5.0	[16]
Hg ²⁺	Magnetic nanoparticles doped with 1,5-diphenylcarbazine	44	<6	[19]
Hg ²⁺	Silica gel modified with 2-(2-oxoethyl)hydrazine carbothioamide	37.5	3	[20]
Hg ²⁺ ,	resins based on poly (methylmethacrylate-co-maleic anhydride)	63	3	[21]
Hg ²⁺	thiol wheat straw	72.46	4-7	[22]
Hg ²⁺	Rhodamine hydrazide modifying Fe ₃ O ₄ microspheres	7.5	-	[23]
Hg ²⁺ ,	carbohydrazide-modified cellulose	64	6	Present work

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