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RESEARCH ARTICLE

SOLID-PHASE EXTRACTION OF CU^{2+}, CD^{2+} AND PB^{2+}FROM WATER SAMPLES WITHTETRACYCLINE MODIFIED CELLULOSE NANOPARTICLES.

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Manuscript Info *Abstract*

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In our study, cellulose nanoparticles customized with tetracycline were produced and characterized by several instrumental techniques such as scanning electron microscopy (SEM), elemental analysis and FTIR. The modified cellulose nanoparticles were employed for removing of and from aqueous solution. Effect of several essential parameters including temperature, pH, adsorption instances and adsorbate concentration had been examined to evaluate the optimum adsorption condition. Chemical adsorption as the rate limiting step was confirmed, where the adsorption kinetics followed the second-order kinetic model. Also, the adsorption isotherm experiments showed the best fit with Langmuir model with maximum adsorption capacities of Cu^{2+}, Cd^{2+} and $Pb^{2+}$with cellulose modified with tetracycline. Comparing to the solvent extraction method an analytical applications of the present method to real samples containing were used and the results were good satisfied.

Introduction:-

Drinking water quality continues to be aserious problem through the fast increase regarding professional activities similar to fertilizers, metal architecture, paints, batteries, pigments;mining, electroplating and also printing models havehigh concentrations metallic ions. The pollutionof drinking water resources by toxic materials isreported as a serious threat regarding to their instant toxicity due to their accumulationin the food chain even at low concentration, causinghazardous effects to marine life along with animal, plants and man health. Toxic heavy metal ions are mainly produced from mercury, lead, radium, cobalt, arsenic, copper varieties, and so forth still to pay to the ability of these pollutants to cause severe health problems [1-6]. Modern separation techniquessuch as anticipation, adsorption, ion exchange, membrane tissue layer processes, and other methods, have been selectively get rid of the metallic ions from dilute wastewaters and professional process channels fields are continually needed [7-12]. Particularly, adsorption has been regarded as a powerful an efficient and economical way of removal of heavy metal ions from wastewaters. Low-cost sorbents has been considerable attention in considerably reducing the expense of price tag on an adsorption process.

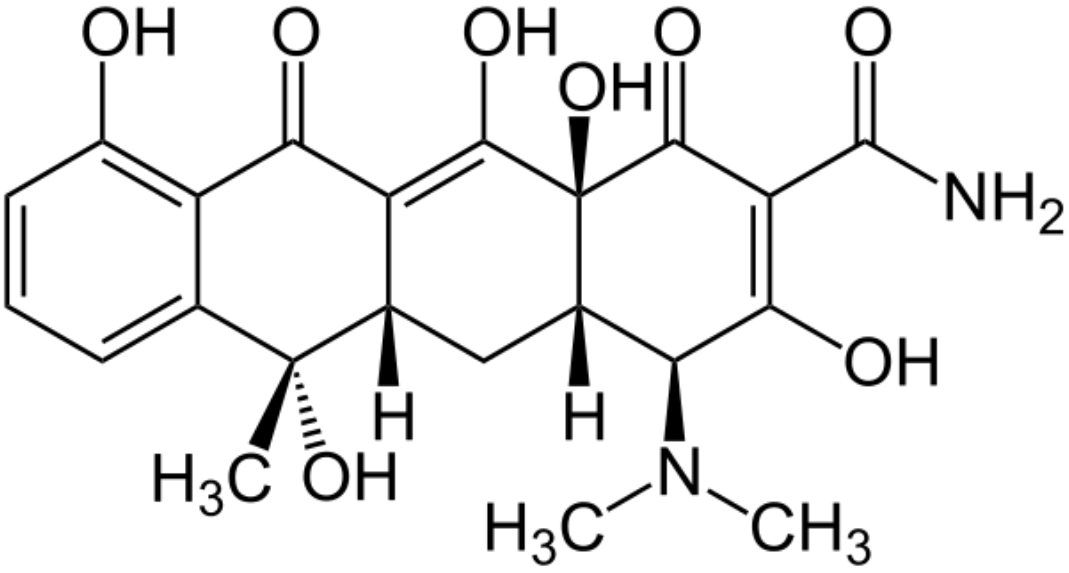
Interestsincreased recently towards the chelating fibersfor enriching and getting rid of heavy metal ions from aqueous solutions. Chelating fibersare incredibly efficient materials due to large adsorption capacity and high selectivity in comparison to other adsorbents plus they are generally also easy to create. This is certainly mainly could be related tohigh adsorption kinetics, the large external specific surface areas, insertof active functional groupings and low cost of these polymer fibers [13-15].

Cellulose is a renewableand natural polymer;it is composed of contentious -D-glucopyranose unitsconnected with OH group of C1 and C4 carbon atoms via covalent bonds[16].Numerous studies were carried out on improvements of physical properties and reactivity of cellulose as a sorbent for metal ions via chemical modification onto the

surface, where it was reported previously, that unmodified cellulose has low stability and poor adsorption capacity[17, 18].

Selective periodate oxidation is one of the most important newly used procedures for cellulose functionalization [19].

Tetracycline is an antibiotic used to treat a many bacterial infections likeacne and rosacea. In the past it was essential in decreasing the number of deaths caused bycholera



Scheme 1:-Tetracycline

In our work, chlorinated cellulose nano-particles weremodified with tetracycline into (Cell-TetrcyclineNPs). The produced nano-particleswereutilized for the preconcentration of some heavy metal ions from aqueous solutions by batch adsorption technique. Essential parameters were studied and optimized. Then, tested method was utilizedto preconcentrate these metal ions in real water samples prior to their determination by spectrophotometric tools.

In the present study, modified cellulose nanoparticles were prepared and fully characterized using various instrumental techniques. The binding and selectivity studies of the fibers has been performed to optimize the different factors affecting the adsorption behavior such as pH, shaking time, initial concentration of metal ions, and temperature. The adsorption kinetics and thermodynamic parameters of the uptake process were also calculated.

Experimental:-

Reagents:-

Analytical reagent-grade chemicals and distilled water were used in all experiments. Cellulose powder from sigma aldrich and used without purification. Used glassware was kept in 10% v/v HNO_3 solution. All glassware werecleaned with distilled water and dried in an oven. (500 mg L^{-1}) stock solutions were prepared by dissolving definite amounts of cadmium chloride, copper chloride and lead nitrate in doubly distilled water acidified with the corresponding acid.

Chlorination of cellulose:-

Cellulose was chlorinated by thionylchlorideas described previously.[22]

Addthionyl chloride ($SOCl_2$) slowly with constant stirring to suspension of cellulose powder in 200ml dimethyl formaldehyde (DMF) .The reaction mixture was heated for four hoursat 80^oC.The white product was Filter and the precipitate washed several times with ammonium hydroxide (10%). until pH was arrived to 7 neutrality .followedby washing with water.The final product was dried in oven.

Synthesis of Cell-tetracycline:-

Cell-tetracyclinewas prepared by the following procedure. tetracycline cellulose modified prepared by refluxing (1:1) 2g of chloro cellulose with 2g tetracycline hydrochloride with same amount of sodium hydroxide dissolve in 10 ml of diluted water in a little amount of absolute acetone by reflux for 4 hr.thenfiltered the precipitated and washed several times with bi- distilled water .dried the stored .

Instrumentation:-

UV /VIS spectrometry Libra S12 (England)UV and VIS spectrophotometric measurements were done for cadmium, copper and lead measurements. The solution pH was measured using digital pH meter (Hanna instrument model HI 8519, Italy). Fourier transform infrared (FT-IR) spectra were measured on Nicolet i10 FTIR spectrometer in the range of 4000 to 400 cm^{-1}. Scanning electron microscope (SEM, Quanta 250 FEG, FEI Company, USA) at an accelerating voltage of 30 kV was used for evaluation of surface morphology and particle size determination.The specific surface area of the cellulose tetracycline was measured by the BET-method [23] (adsorption gas N_2, carrier gas He, heating temperature 150 °C).

Metal ion uptake experiments using batch method:-

Adsorption and desorption experiments:-

Set of procedures were performed to judge the removal of metallic ions using Cell-tetracycline. In almost all of the experiments, 0.02 g of the studied modified cellulose were put in 100 cubic centimeters stoppered bottles containing twenty-five mL metal ions aqueous solution with main focus 20 mg/L other than case of adsorbent isotherm studies where the initial metal ions focus on ranged between 10-100 mg/L. Thermodynamic studies where the concentration was (20 mg/L), at pH 2-8, at 30°C (but for the effect of temperature studies the temperature ranged between 20-50°C) and for 3h (except for the kinetic studies where the contact time changed from 10-120 min). All the containers bottles have been agitated using orbital shaker at regular rate of 150 rpm perminute. Then, the fibers have been eliminated and the rest metal ion content was determined using atomic absorption.

Both Eq (1) and Eq (2) were employed to evaluate the quantity of metals adsorbed per one gram of the adsorption and the percent associated with metal ions, correspondingly.

qe = (Ci-Ce)V/W (1)

Where qe (mg/g) adsorbent capacity; Ci (mg/L) and Ce (mg/L) initial and equilibrated metal ion concentrations, respectively, V (L) volume level of added solution and W (g) the mass of the adsorbent (dry).

Percent removal (%) = (Ci-Ce) x 100 /Ci (2)

Analytical application of the current method:-

First of all we added 0. 5 g of potassium persulphate to at one liter of aliqout and then we added 5 ml of H_2SO_4, and heated for 2 h at 95°C to be sure that all organic matter which may be present has recently been digested. 1 g of modified cellulose has recently been added to the test in two times and the pH value was adjusted to (3-5) shaking occurs, after that elution occurs using 20 ml of one particular (0.1mol/ L) HCl for the modified cellulose.

As described previously separation by solvent extraction were performed for Preconcentration. The pH level of 1 lite of the aliquot was controlled to practically 3- 5 using 0. 1 M H_2SO_4, 5 ml of ammonium pyrolidinedithiocarbamate (APDC) solution was added, shaking occurs well for few seconds to complete chelation process. To this solution, 50 ml (MIBK), has been added. The obtained organic layer obtained and elements under test are identified using AA

Results and discussion:-

Characterization of the polymeric fiber samples:-

Element analysis:-

The resultswhich have been obtained by elemental analysisof native cellulose and**Cell-tetracycline**are shown in Table 1. It is visibly shown that, after thechlorination step and modification of cellulose, the content of nitrogen show visible increases. From the obtained results the insertion of the tetracycline parts onto the chlorinated modified cellulose is shown.

Infra red spectra:-

IR used to confirm the modification of cellulose with tetracycline. The IR spectra of the cellulose, chlorinated cellulose, and **Cell-tetracycline** are shown in Fig. 1. Cellulose displayed the main characteristics peaks at 1433 cm^{-1} (-CH_2 bending and -OCH in-plane bending), 2902 cm^{-1} (C-H stretching), 3346 cm^{-1} (-OH stretching),1060 cm^{-1} (C-O-C stretching), 1370 cm^{-1} (-CH bending) and 668 cm^{-1} (C–OH out-of-plane bending) as reported previously. Upon chlorination, new peak observed at 750 cm^{-1}, which is due to the chloride group which is formed[22]. After modification with tetracycline, new peak appeared at 1739 cm^{-1}characteristic to imine unit stretching vibration, confirming the formation of new carbonyl group[23].

Scan electron microscope:-

Bothraw and modified cellulose which were examined by SEM to get more information about the morphology and size of produced particles. As shown in Fig. 2a, the raw cellulose is comprised of aggregated micro-fibers, then afterchlorinationusingthionyl chloride; the cellulose microfiberschanged to nanospheres with average size of 35 nm as shown in Fig 2b. Moreover,after coupling with tetracycline; it can be observed that the shape ofnanospheresdidn't change (Fig 2c). According to the results of BET surface area studies, **Cell-tetracycline**have a surface area of 178 $m^2 g^{-1}$, this relatively high surface area is due to its nanostructure.

Effect ofpH:-

It was shownthatan important role of the initial pH of the aqueous solution which affected on the chemically sorption[25].Initial pH value,affected on the uptake of [**Cu^{2+}, Cd^{2+} and Pb^{2+}**]using **Cell-tetracycline** has been tested in pH range 2-8, before the precipitation limits, as shown in Fig.3. The uptakeof [**Cu^{2+}, Cd^{2+} and Pb^{2+}**]adsorptionsweregradually, increased by increasing pH value. The adsorption occurred through coordination between both the active sitespresent in the modified cellulose and the metal ions.The competition of H^+ with metal ions, for adsorption active sites will subsequently lower the ability of these, sites to coordinate, with [**Cu^{2+}, Cd^{2+} and Pb^{2+}**]at lower pH.

The thermodynamic studies:-

The thermodynamicsuch asenthalpy (ΔH°) and free energy (ΔG^{o}), entropy (ΔS°) of the adsorption process of [**Cu^{2+}, Cd^{2+} and Pb^{2+}**]by Cell-**tetracycline** as chelating agents.Theparameters of thermodynamic and equilibrium constant were shown.

$$K_C = C_{ad} / C_e \qquad (3)$$

Where C_{ad} is the concentration of metal ions adsorbed on the modified cellulose at equilibrium (mg/g) and C_e is the equilibrium concentration (mg / L).

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

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

That the gas constant R (8.31 J/mol K)

The values of ΔS^{o}_{ads} and ΔH^{o}_{ads} has been estimated from the slope ($-\Delta H^{o}_{ads}$ /R) and intercept (ΔS^{o}_{ads} /R) of the $\ln K_c$ vs. 1/T

Table (2) lists all the obtained thermodynamic parameters. As shown negative ΔG^{o}_{ads} values show the thermodynamic feasibility,(spontaneous process) standard free energy showdecreasing by raising temperature show that the uptake of metal ions from solution is favorable at lower temperature.

The capacity of adsorption of the metal ions decreased with increasing temperature. This might be due to the low interaction, between the metal ions and the active groups

Kinetic studies:-

Fig. 7 shows the kinetics of the adsorption of the studied, metal ions [Cu^{2+}, Cd^{2+} and Pb^{2+}]by **Cell-tetracycline**. The uptake–time curves show that the maximum uptake follows the order [Cu^{2+}, Cd^{2+} and Pb^{2+}]at all-time intervals. For Cu^{2+} ions, the kinetic curve given that the adsorption was, firstlyfast, then reached equilibrium after approximately 100 min. **Cd^{2+}andPb^{2+}** ions, adsorption reached equilibrium in 100 and 110 min, respectively and remained, constant until the end of the experiment.

The pseudo-first-order equation (Eq. (6)) and the pseudo-second-order equation (Eq. (7)) are the most frequently has been used

$$1/qt = k1/q_e t + 1/qe \qquad (6)$$

$t/qt= 1/k2q_e^2+ (1/qe)t$ (7)

whereq_t ($mg.g^{-1}$) andq_e ($mg .g^{-1}$) are the adsorption capacities at equilibrium and at time t (min), respectively. K_1 is the of pseudo-first-order adsorptionrate constant, k_2 the of pseudo-second-order adsorption rate constant.

We determine, k and q_e were determined together and values which is near to experimental value is more favored, from determination of the value of correlation coefficient, which is preferred when the value of correlation coefficient is near to unity and also compare

Table (3) shows the obtained parameters and we can be noticed that pseudo-second-order equation exhibited the fit withdata which obtainedexperimentally.

According to the correlation coefficients (R^2), the pseudo-2nd-order, equation is the model that furthered the best fit for the experimental kinetic data; chemical sorption is the rate-limiting step.

Adsorption isotherms:-

The obtained results were studied, with both Freundlich and Langmuir isotherm models and all the parameters have been shown in Table (4). As shown; model ofLangmuir showed the best fit for theobtained data from the correlation coefficient values. The maximum adsorption capacities for [Cu^{2+}, Cd^{2+} and Pb^{2+}]Cell-tetracyclineare 77, 61 and 50 (mg/ g) respectively.

The adsorption process suitability evaluated by calculating the separation factor constant (R_L): $R_L > 1.0$, unsuitable; $R_L = 1$, linear; $0 < R_L < 1$, suitable; $R_L = 0$, irreversible. The R_L value can be estimated according to the following equation (8).

$$R_L = 1/ (1+C_oK_L) \quad (8)$$

The values of R_L lie between 0.012and 0.54, indicating the suitability of the **Cell-tetracycline**under study as adsorbents for metals under study from aqueous solution.

Fibers reusability:-

From examining the reusing of modified cellulose, five cycles of adsorption-desorption have been done under optimum conditions and the results were presented in Table 5. It is shown that the uptake efficiency of the **Cell-tetracycline**modified cellulose didn't decrease. After the fifth cycle, the modified cellulose maintains about 87% of its efficiency. According to these results, it is expected that **Cell-tetracycline**fibers would be a promising adsorbent for fast removal of [Cu^{2+}, Cd^{2+} and Pb^{2+}]from water

Analytical applications of the present method:-

The pH, alkalinity, TDO, and TDS of some different water stations around EL- Dakahlia governorate are shown in table (7)

Statistical evaluation for [Cu2+, Cd2+ and Pb2+]in natural water samplescollected from several locations from TheNile in Cairoand El-Dakahlia Governorate at 26th April 2016 after pre-concentration by (**Cell-tetracycline**) method (1) and solventextraction method (2)

The comparison between the present method (1) and the solvent extraction method (2) is shown in Table 7

From the calculated pooled estimate of standard deviation and $[t]_2$ test (table 7), it's clear that the present results are greed with the standard solvent extraction. Also all the calculated two tailed F –test of all water samples are acceptable The F-test also shows that all water samples are not subjected to random errors

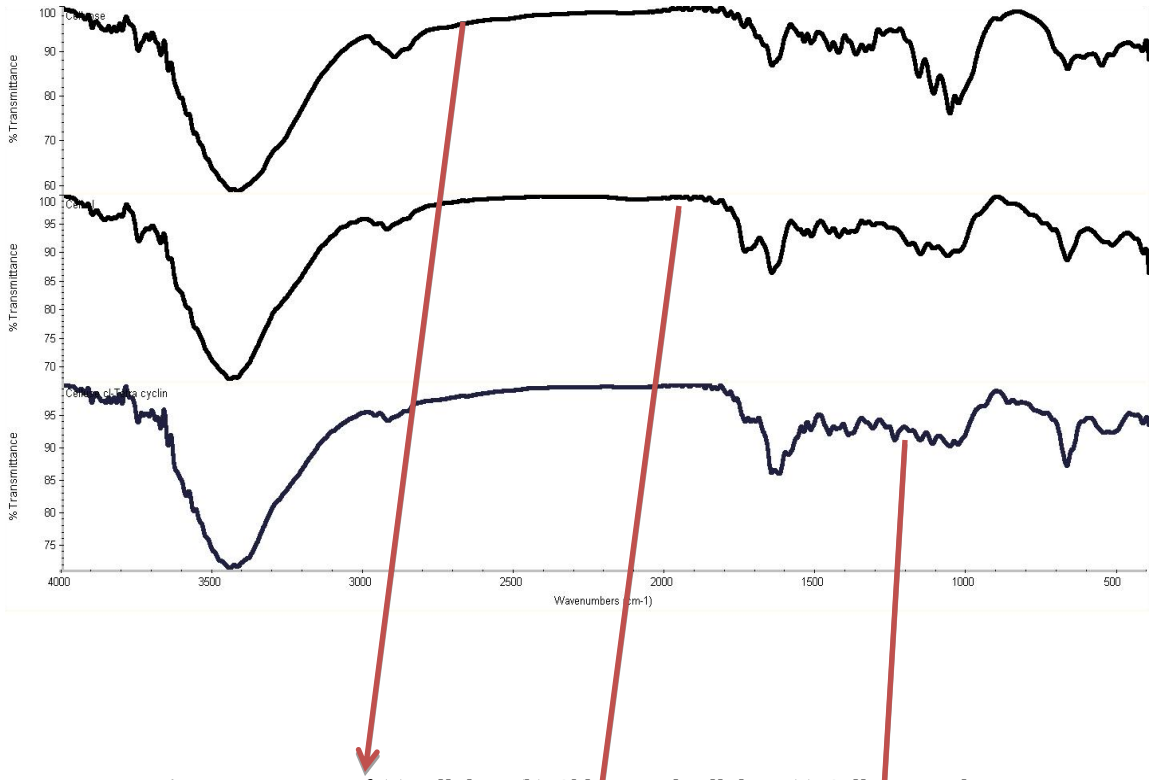
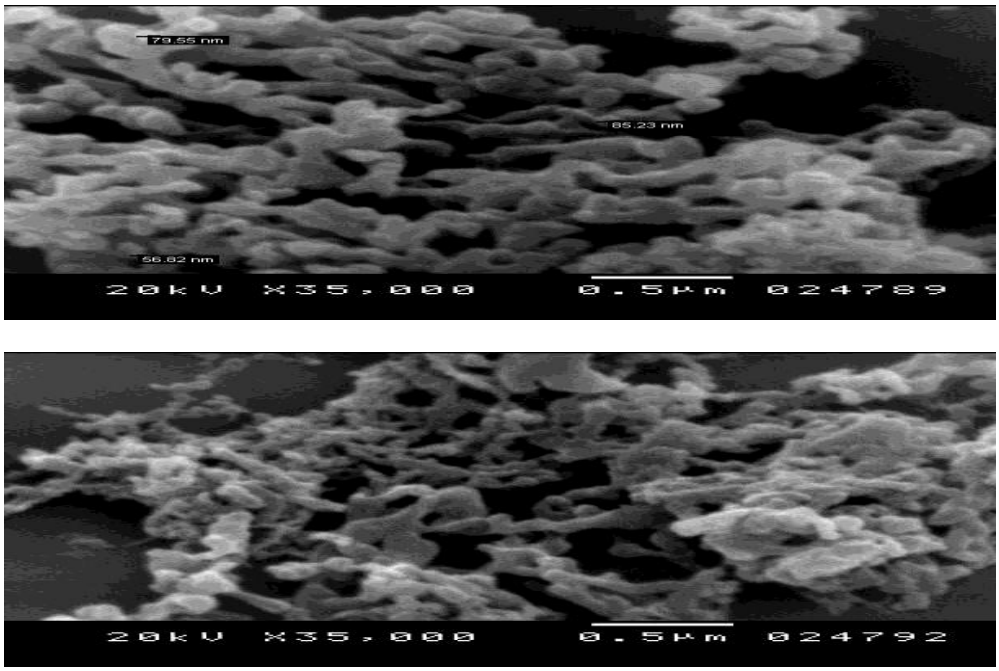
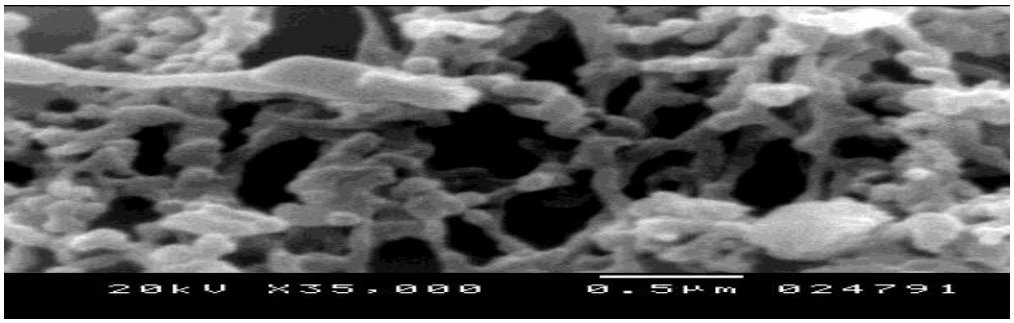


Fig. 1:-IR spectra of (a) cellulose,(b) Chlorinated cellulose,(c) Cell-Tetracycline



(a)



(b)

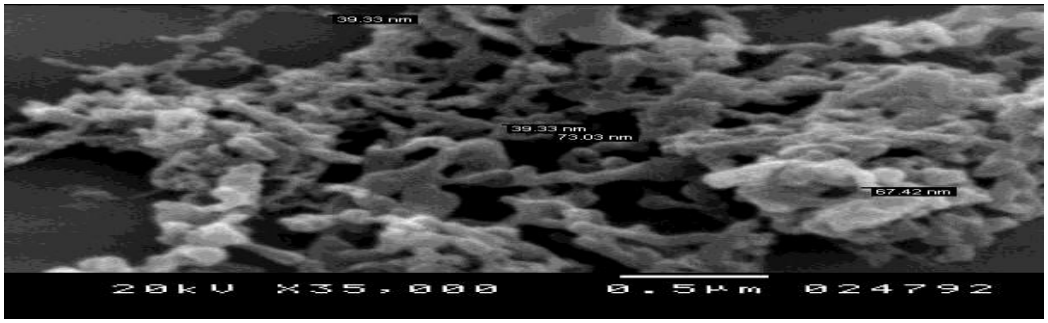


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Fig. 2:- SEMsimage of (a) cellulose, (b) chlorinated cellulose, (c) Cell-tetracycline.

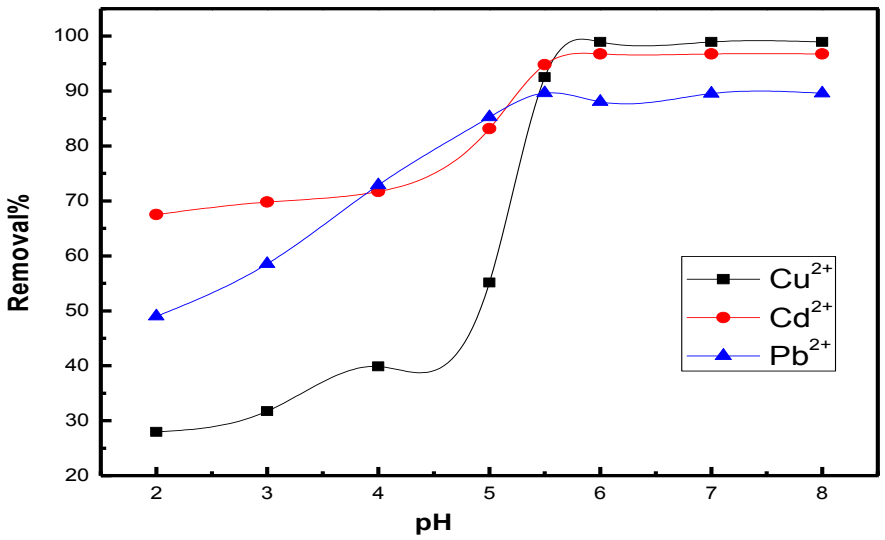

Fig. 3:-Effect of pH on the uptake of [**Cu^{2+}, Cd^{2+} and Pb^{2+}**]ions by**Cell-tetracycline** (25 ml (20 mg/L) , adsorbent 0,02 g, contact time 3 h, shaking rate 150 rpm, 25^0C).

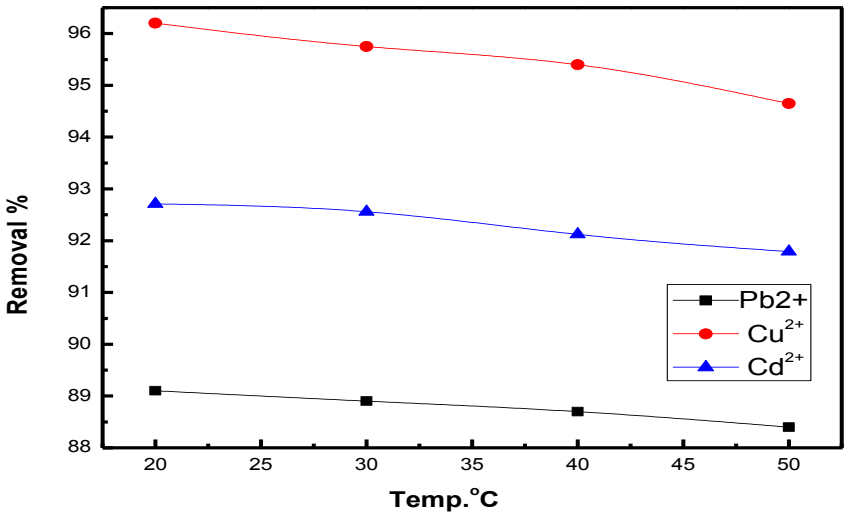

Fig. 4:- Plot of percent removalas a function of temperature (T) for the adsorption of [**Cu^{2+}, Cd^{2+} and Pb^{2+}**]

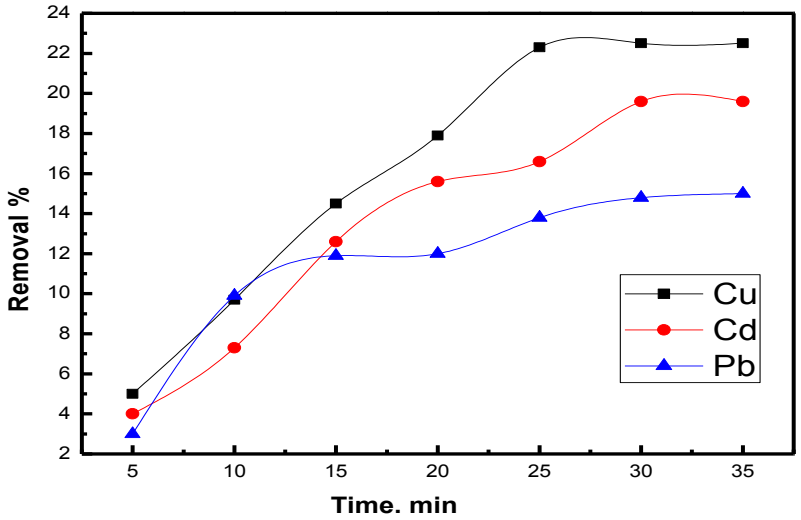

Fig. 5:- Effect of contact time on the uptake of[**Cu^{2+}, Cd^{2+} and Pb^{2+}**]ions by **Cell-tetracycline**(25 ml(35 mg/L), adsorbent . 0,02 g, pH 7-8, shaking rate 150 rpm, 25°C).

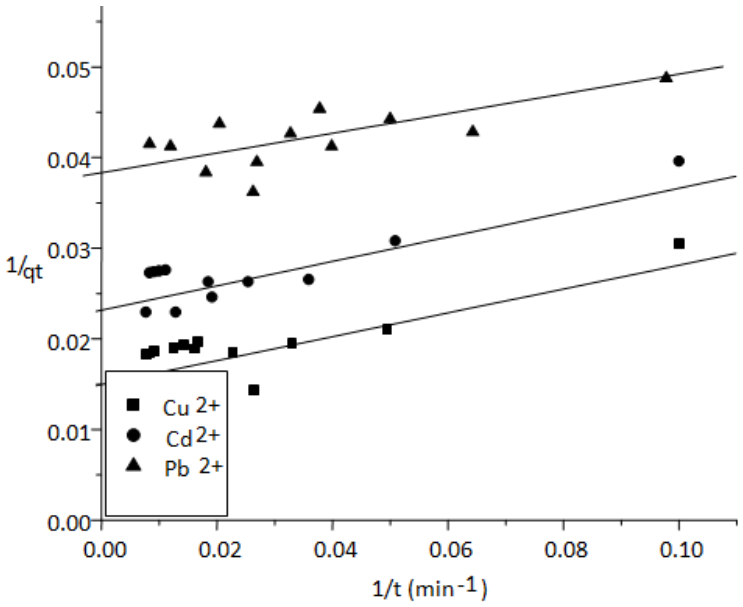

Fig. 6:- pseudo – first kinetics of the uptake of [**Cu^{2+}, Cd^{2+} and Pb^{2+}**]on **Cell-tetracycline**

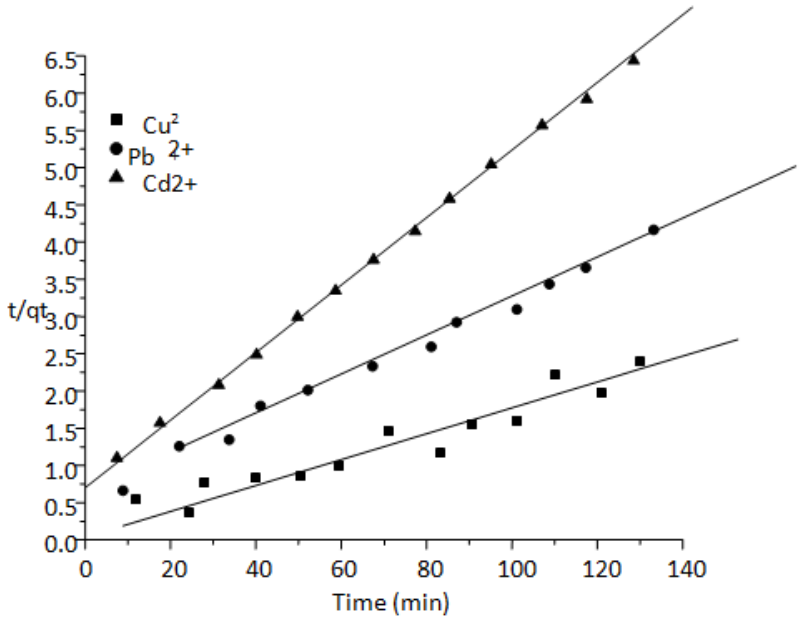

Fig. 7:-pseudo second kinetics of the uptake of [**Cu^{2+}, Cd^{2+} and Pb^{2+}**]on**Cell-tetracycline.**

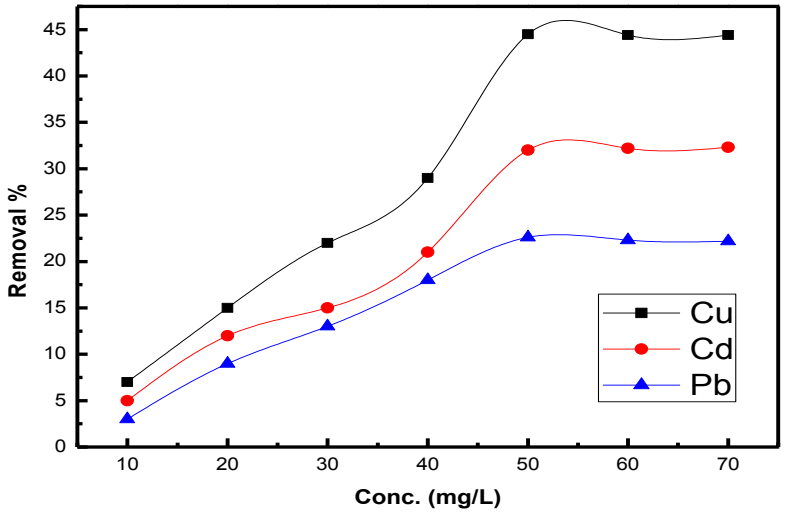

Fig.8:-Adsorption isotherms of [**Cu^{2+}, Cd^{2+} and Pb^{2+}**]ions by **Cell-tetracycline**(initial concentration (10-50) mg/L, adsorbent 0.02g pH 7-8, shaking rate 150 rpmand 25°C).

Table 1:- Elemental analysis of cellulose andCell-tetracycline.

Fibers	C(%)	H(%)	N(%)
cellulose	36.58	4.01	--------
Cell-tetracycline	39.63	5.38	0.21

Table 2:- Thermodynamic parameters for the adsorption of [Cu^{2+}, Cd^{2+} and Pb^{2+}]byCell-tetracycline.

System	K_c			$-\Delta G^o_{ads}$ (KJ/mol)			ΔH^o_{ads} (KJ/mol)	ΔS^o_{ads} (J/mol K)
	293 K	303 K	313 K	293 K	303 K	313 K		
Cu- Cell-tetracycline	210	208	196	19.765	19.098	13.987	-22.08	-41.654
Cd- Cell-tetracycline	225	210	189	11.87	10.99	10.910	-19.573	-32.985
Pb- Cell-tetracycline	170	150	121	10.98	11.5	9.4	-14.623	-32.823

Table3:-Kinetic parameters for adsorptionof [**Cu^{2+}, Cd^{2+} and Pb^{2+}**]by**Cell-tetracycline.**

Fibers	First-order model		
Cu- Cell-tetracycline	k_1 (min^{-1})	q_{e1}(mg/g)	R^2
	2.2	17±3	0.9117
Cd- Cell-tetracycline	6.3	13±2	0.9337
Pb- Cell-tetracycline	3.3	12±4	0.9227
Fibers	Second-order model		
Cu- Cell-tetracycline	k_2 (g/(mg min))	q_{e2} (mg/g)	R^2
	1.1×10^{-3}	19± 2	0.9987
Cd- Cell-tetracycline	1.3×10^{-3}	13± 3	0.9988
Pb- Cell-tetracycline	0.7×10^{-3}	10± 2	0.995

Table .4:-Physico-chemical adsorption of [**Cu^{2+}, Cd^{2+} and Pb^{2+}**]ions by**Cell-tetracycline.**

Fibers	**Langmuir isotherm constants**			
Cu- Cell-tetracycline	**K_L(L/g)**	**q_m(mg/g)**	**R^2**	**R_L**
	$13x10^{-2}$	**17**	**0.996**	**(0.012-0.541)**
Cd- Cell-tetracycline	**$11x10^{-2}$**	**14**	**0.97**	**(0.013-0.451)**
Pb- Cell-tetracycline	**$10x10^{-2}$**	**10**	**0.988**	**(0.015-0.451)**
Fibers	**Freundlich isotherm constants**			
Cu- Cell-tetracycline	**K_F**	**n**	**R^2**	
	13.452	**2.9**	**0.8988**	
Cd- Cell-tetracycline	**11.385**	**2.2**	**0.9187**	
Pb- Cell-tetracycline	**7.772**	**2.1**	**0.9212**	

Table.5:- Repeated adsorption [**Cu^{2+}, Cd^{2+} and Pb^{2+}**]ions by **Cell-tetracycline** (initial concentration 20 mg/L, **Cell-tetracycline** 0.02 g, pH3-8.0, contact time 3h, shaking rate 150 rpm, 25◦C)

Cycle number	**Recovery(%) by Cell-tetracycline**		
	Cu^{2+}	**Cd^{2+}**	**Pb^{2+}**
1	**100**	**100**	**100**
2	**98.9**	**98.9**	**96.8**
3	**96.4**	**98.6**	**97.2**
4	**95.2**	**95.3**	**95.4**
5	**89.8**	**86.5**	**89.6**

Table 6:- Determination of pH, alkalinity, DO and TDS of some different water samples from El Dakahlia water stations:

Parameters Locations	**Temp, °C**	**pH**	**Alkalinity, $CaCO_3$ ppm**	**TDO ppm**	**TDS ppm**
Mansoura water station(a)	**25**	**7.99**	**165**	**5.7**	**303**
The nile water(d)	**31**	**6.9**	**122**	**5.5**	**412**
Intake of Hagayza water station(a)	**32**	**7.69**	**154**	**5.4**	**317**
El Mansoura city (b)	**31.1**	**7.22**	**120**	**8.2**	**314**

Table 7:- Comparison between the present method (1) and solvent extraction method (2)

Sample location	**Method (1)**		**Method (2)**		**Sp***	**[t]$_2$****	**Two-tailed (F-test)[a]**
	X_1 µg/ml	**S_1 µg/ml**	**X_2µg/ml**	**S_2 µg/ml**			
				Cu^{2+}			
Mansoura water station(d), El-Dakahlia Governorate	**0.22**	**0.03**	**0.25**	**0.025**	**0.027**	**2.29**	**1.44**
The Nile water	**0.45**	**0.04**	**0.42**	**0.038**	**0.039**	**0.83**	**1.10**
				Cd^{2+}			
Intake of Mansoura water station(a)	**1.8**	**0.15**	**1.9**	**0.14**	**0.145**	**1.11**	**1.14**
The Nile water	**3.2**	**0.21**	**3.21**	**0.07**	**0.176**	**0.09**	**4.16**
				Pb^{2+}			
Intake of Mansoura water station(a)	**0.39**	**0.08**	**0.41**	**0.07**	**0.075**	**1.27**	**1.30**
The Nile water	**0.42**	**0.075**	**0.44**	**0.07**	**0.072**	**1.10**	**1.14**

* $S_P = \sqrt{\{(n_1-1)s_1^{\,2} + (n_2-1)s_2^{\,2}\} / (n_1+n_2-2)}$

** $|t|_2 = (\overline{X}_1 - \overline{X}_2) S_P \sqrt{1/n_1 + 1/n_2}$, P=0.05, n=10 for the sum of the two methods is equal to 2.31

a $-F_{4,4} = S_1^{\,2} / S_2^{\,2}$, n=5 is equal to 9.605(two tailed F-test)

Conclusions:-

In this work, novel modified cellulose (**Cell-tetracycline**) was prepared and characterized using various instrumental techniques. The thermodynamic studies indicated that the adsorption was exothermic in nature and spontaneous at all studied temperatures.

The adsorption kinetics of metal ions onto **Cell-tetracycline**was fast and followed the pseudo-second order model confirming the adsorption through the chemical coordination mechanism. Also, Langmuir isotherm model was well fitted with the experimental data, which show the monolayer adsorption of metal ions.
The present method was applied to real samples taken from different water stations aroundEl-Dakahlia Governorateandcairo compared with the standard solvent extraction method. The obtained results were satisfied and agreed with the standard solvent extraction method

References:-

1. B. Gao, Y. Gao, Y. Li, Chem. Eng. J. 158 (2010) 542–549.
2. G. Cimino, C. Caristi, Biol. Waste 33 (1990) 201–210.
3. D. Mohan, K.P. Singh, Water Res. 36 (2002) 2304–2318.
4. T.K. Sen, S.P. Mahajan, K.C. Khilar, Physico. and Eng. Asp 211 (2002) 91–102.
5. A.B. Perez-Martin, V.M. Zapata, J.F. Ortuno, M. Aguilar, J. Saez, M. Llorens, J. Hazard. Mater. 139 (2007) 122–131.
6. A. Murugesan, L. Ravikumar, V. SathyaSelvaBala, P. SenthilKumar , T. Vidhyadevi, S. Dinesh Kirupha, S.S. Kalaivani, S. Krithiga, S. Sivanesan.. Desalination 271 (2011) 199-208.
7. R.Y. Ning, Arsenic removed by reverse osmosis, Desalination 143 (2002) 237–241.
8. U.V. Gunten, Water Res. 37 (2003) 1443–1467.
9. X. Chen, G. Chen, P.L. Yue, Environ. Sci. Technol. 36 (2002) 778–783.
10. Z. Hu, L. Lei, Y. Li, Y. Ni, Sep. Purif. Technol. 31 (2003) 13–18.
11. Z. Reddad, C. Gerente, Y. Andres, J.F. Thibault, P. Le Cloirec, Water Res. 37 (2003) 3983–3991.
12. W. Ciesielski, C.Y. Lii, M.T.Yen, P. TomasikCarbohyd. Polym. 51 (2003) 47–56.
13. S.B. Deng, R.B. Bai, J.P. Chen, J. Colloid Interface Sci. 260 (2003) 265–272.
14. S. Deng, R. Bai, Water.Res. 38 (2004) 2424–2432.
15. M. Yigitoglu, M. Arslan, J. Hazard. Mater. 166 (2009) 435–444.
16. D.L. Kaplan: Biopolymers from renewable resources. New York: Springer; 1998.
17. F.E. Okieimen, C.E. Sogbaike, J.E. Ebhoaye, Sep. Purif. Technol., **44**, 2005, 85-89.
18. D.W. O'Connell, C. Birkinshaw, T.F. O'Dwyer, Bioresour. Technol.,**99**, 2008, 6709-6724
19. Kim, U.-J., Kuga, S., Wada, M., Okano, T., & Kondo, T. 1, (2000). Biomacromolecules, 488–492.
20. Nikolic, T., Kostic, M., Praskalo, J., Pejic, B., Petronijevic, Z., Skundric, P. (2010).
21. M. G. Abd El-Wahed, M. S. Refat, and S. M. El-Megharbel, Spectrochim. Acta, Part A, 2008, **70**, 916-922.
22. M. Monier, I.M.M. Kenawy, M.A. Hashem, Carbohydr.Polym., 2014, **106**, 49-59
23. S. Brunauer, P. Emmett, E. Teller, J. Am. Chem. Soc., 1938, **60**, 309-319.
24. Standard methods for the examination of water and waste water. 22 Edition, Reviewed by Standard Methods Committee, 2011, Edited by Eugene W. Rice Rodger, B. Baird Andrew, D. Eaton Lenor and S. Clesceri
25. M.Monier, & Abdel-Latif, D. A. Chem. Eng. Journal, 221, 2013,452–460.