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RESEARCH ARTICLE

Solid-phase extraction of Al^{3+}, Cr^{3+} and Fe^{3+} from water samples with folic acid modified cellulose nanoparticles

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Abstract

In the present study, cellulose nanoparticles modified with folic acid were synthesized and characterized using some instrumental techniques such as elemental analysis, scanning electron microscopy (SEM) and FTIR. The modified cellulose nanoparticles were employed for removal of Al^{3+}, Cr^{3+} and $Fe^{3+}$from aqueous solution. Someimportant parameters such as pH, adsorbate concentration, temperature and adsorption times were studied to estimate the optimum adsorption condition. According to results, adsorption kinetics followed the second-order kinetic model indicating that the chemical adsorption is the rate limiting step. Also, Langmuir model showed the best fit in adsorption isotherm experiments with maximum adsorption capacities of 88, 68 and 56 mg/g for Fe^{3+}, Al^{3+} and $Cr^{3+}$with cellulose nanoparticles modified with folic acid .An analytical applications of the present method compared with the solvent extraction method to real samples containing Al^{3+}, Cr^{3+} and Fe^{3+}were used and the results were satisfied.

INTRODUCTION

Water pollution continues to be an serious problem through the rapid growing of global industrial activities like to metal fabrication, fertilizers, pigments,paints, electroplating, mining,batteries, extracting and also printing tools that contain high concentrations of metal ions. Water sources contaminated by toxic metals are considered as a serious threat to humanity due totheir non-biocompatibility and their harmful toxicity. Even at lower concentration, these heavy metal ions can be accumulated through the food chain leading to harmful effects on the aquatic life as well as toman health,plant life and animal. Toxic heavy metal ions are mainly derived from mercury, cobalt, cadmium, lead, arsenic, copper species, etc. owing to the ability of these species to cause serious health problem [1–6].

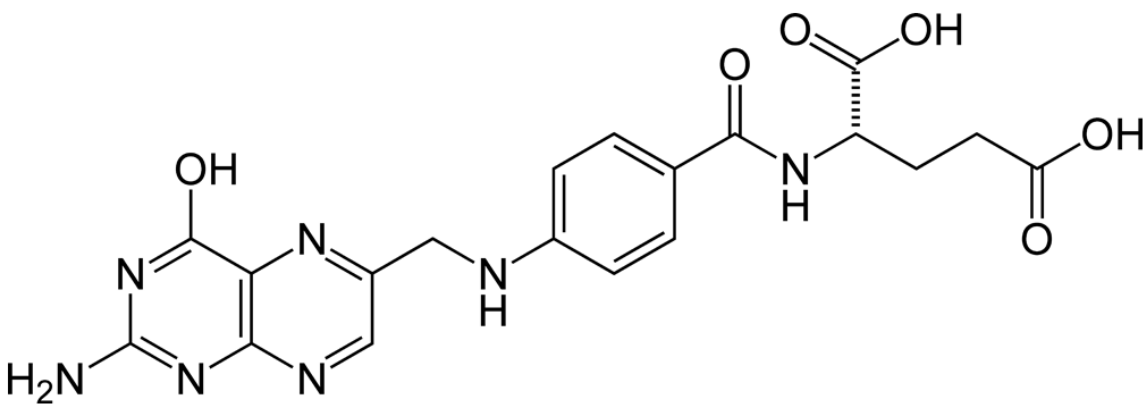
Numerous techniques such as precipitation, adsorption, ion exchange and membrane processes have been applied for elimination of heavy metal ions[7–12].Especially, adsorption has been considered as an economic and effective method for removal of heavy metal ions from wastewaters. Low-cost sorbents gained a considerable attention in reducing the cost of an adsorption process.

Recently, chelating fibers are applied widely for removing and enriching heavy metal ions from aqueous solutions. Chelating fibers are very effective regarding to large adsorption capacity, high selectivity and can be regenerated easily. This could be mainly attributed to the high adsorption kinetics, relatively large external specific surface areas, low cost of these polymer fibers and insertion of active functional groups [13-15].

Cellulose is the most abundant renewable natural polymer on the word. It composed of repeating β-D-glucopyranose units, covalently linked with OH group of C4 and C1 carbon atoms.[16] The unmodified cellulose has poor adsorption capacity and low stability.[17] Therefore, several studies have attempted on improvements of reactivity and physical properties of cellulose as a sorbent for metal ions by introducing chemical modifiers onto its surface.[18]

Selective periodate oxidation is one of the most important frequently used procedures for cellulose functionalization [19]. In this oxidation reaction, the C2-C3 bond of the glucopyranoside ring will be selectively cleaved and converted into two aldehyde groups, which will provide an additional functionality for further cellulose modification with maintaining the mechanical and morphological properties of the fibers [20].

Folic acid (Scheme 1, *N*-[4-[[(2-amino-1,4-dihydro-4-oxo-6-pteridinyl)methyl]amino]benzoyl]-L-glutamic acid) is a water-soluble B vitamin that helps the body to build healthy cells. Folic acid is also known to form complexes with metal ions [21], which is due to presence of several functional groups in its structure.



Scheme 1. Structure of folic acid

In this work, new functionalized nano-particles were synthesized by immobilization of folic acid into oxidized cellulose (Cell-FoNPs). The produced modified cellulose was used for the preconcentration of Al^{3+}, Fe^{3+} and $Cr^{3+}$from aqueous solutions by batch mode. The main factors affecting the separation process were studied and optimized.The procedure was applied for the preconcentration of these metal ions in water samples prior to theirdetermination by spectrophotometric determination. To the best of our knowledge, there is no report about the preconcentration of metal ions using cellulose modified with folic acid in the literature.

In the present study, modified cellulose nano-particles 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

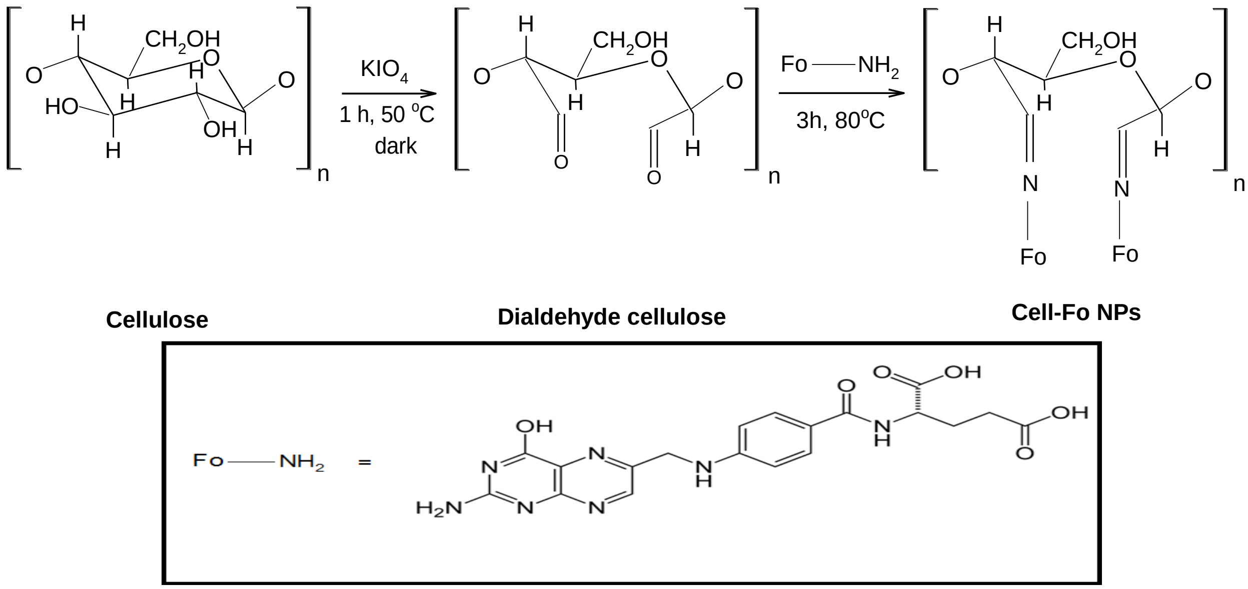
Analytical reagent-grade chemicals and doubly distilled water (Milli-Q water purification system, Millipore, Billerica, MA, USA) were used throughout the experiments. Cellulose powder was purchased from Whatman Chemical Separation Ltd., U.K. and used without any further purification. The laboratory glassware was kept overnight in 10% v/v HNO_3 solution. Before the use, the glassware was washed with doubly distilled water and dried in a dust free environment. The stock solutions of metal ions (1000 mg L^{-1}) were prepared by dissolving appropriate amount of aluminium metal, ferrous ammonium sulphate and chromium sulphate in doubly distilled water acidified with thecorresponding acid.Working solutions were prepared daily from the stock solution by dilutions with doubly distilled water.

Periodate oxidation of cellulose

Cellulose was oxidized by potassium periodate as described previously [22]. Two grams of cellulose were soaked in 100 mL 3 g L^{-1} aqueous KIO_4 solution and the mixture was gently shaken for 1 h at 50 ^oC in the dark. The oxidized cellulose was removed and the remaining periodate were eliminated by immersing in 100 mL 1% aqueous ethylene glycol solution and stirring the mixture for 30 min. The oxidized cellulose was washed with absolute ethanol.

Synthesis of Cell-FoNPs

Cell-FoNPs was prepared by the following procedure. The ethanol wet oxidized cellulose was soaked in 100 mL 1% (w/v) alcoholic solution of folic acid and the mixture was refluxed at 80 ^oC for 3 h.The product (Cell-FoNPs)was filtered off, washed ethanol and dried undervacuum at 60^oC for 2 h. The synthetic route of Cell-FoNPsis illustrated in Scheme 2.



Scheme 2.Synthesis of Cell-FoNPs.

Instrumentation

UV /VIS spectrometry Libra S12 (England) UV and VIS spectrophotometric measurements were done for aluminum, iron and chromium 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 HAPNRs was measured by the BET-method [23] (adsorption gas N_2, carrier gas He, heating temperature 150 °C).

2.4. Metal ion uptake experiments using batch method

2.4.1. Adsorption and desorption experiments

Batch procedures were performed to evaluate the removal of metal ions using **Cell-FoNPs**. In most of the experiments, 0.04 g of the studied modified cellulose were placed in 100 mL stoppered bottles containing 40 mL metal ions aqueous solution with main concentration 100 mg/L (except in case of adsorption isotherm studies where the initial metal ions concentration ranged between 10-400 mg/L and thermodynamic studies where the concentration was 40 mg/L), at pH 1-5, at 30°C (except for the temperature effect where the temperature ranged between 20-40°C) and for 3h (except for the kinetic studies where the contact time changed from 10-120 min). All the bottles have been agitated using orbital shaker at constant rate of 150 rpm. 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 amount of metals adsorbed per one gram of the adsorbent and the percent removal of metal ions, respectively.

$$q_e = (C_i\text{-}C_e)V/W \qquad (1)$$

Where q_e(mg/g) adsorption capacity; C_i (mg/L) and C_e (mg/L) initial and equilibrated metal ion concentrations, respectively, V (L) volume of added solution and W (g) the mass of the adsorbent (dry).

$$\text{Percent removal (\%)} = (C_i\text{-}C_e) \times 100 / C_i \qquad (2)$$

2.5. Analytical application of the present method

Firstly we added 0.5 g of potassium per sulphate to 1 litre of aliquot and then we added 5 ml of concentrated H_2SO_4, and heated for 2 h at 95°C to become sure that all organic matter which may be presenthas been digested. 1 g of modified cellulose has been added to the sample in two times and the pH value was adjusted to (3-5) shaking occurs, after that elution occurs using 20 ml of 0.1(mol/ L) HCl for the modified cellulose.

As described previously separation by solvent extraction were performed for Pre-concentration [24] **.**The pH of 1 lite of the aliquot was adjusted to nearly 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 phase was obtained and elements under test are determined using AAS

3. Results and discussion

3.1. Characterization of the polymeric fiber samples

3.1.1. Element analysis

The obtained results from analysis of the elements of native cellulose and**Cell-FoNPs** has been shown in Table 1. It's visible that, after the oxidation step and modification of cellulose, the content of nitrogen show visibly increases. From the obtained results the insertion of the folic acid moieties onto the oxidized modified cellulose is shown.

3.1.2. Infra red spectra

FT-IR was used to ascertain the immobilized folic acid onto the surface of the cellulose. The FT-IR spectra of the original cellulose powder, DAC, folic acid and Cell-FoNPs are shown in Fig. 1.The IR spectrum of raw cellulose displayed the main characteristics peaks of cellulose. Absorbance at 3346 cm^{-1} (-OH stretching), 2902 cm^{-1} (C-H stretching), 1433 cm^{-1} (-CH_2 bending and and -OCH in-plane bending), 1370 cm^{-1} (-CH bending), 1060 cm^{-1} (C-O-C stretching) and 668 cm^{-1} (C–OH out-of-plane bending) are in good agreement with the reported values.[25]Upon periodate oxidation, the spectrum showed a peak at 1714 cm^{-1}, which is due to the carbonyl group which is formed [22]. After coupling with folic acid, the produced Schiff base shows a peak at 1693 cm^{-1} which is characteristic to imine unit stretching vibration, indicating the presence of the newly formed imine linkage..[23]

3.1.3. Scan electron microscope

The morphology and size of the raw and modified cellulose were studied by SEM. Fig. 2a shows SEM of the raw cellulose, it can be concluded that the raw cellulose is comprised of aggregated microfibrils. Oxidation by periodate changes the cellulose microfibrils into nanospheres with average size of 34 nm as illustrated in Fig 2b. Also it can be observed that the nanospheres still maintain their shape after coupling with folic acid (Fig 2c). According to the BET surface area measurements, Cell-FoNPs exhibited a surface area of 178 m^2 g^{-1}. The relatively high surface area of the prepared sorbent is due to its nanostructure.

3.2. Effect of pH

It was seen that an essential role of the initial pH of the aqueous solution which affected on the chemically sorption [25]. Initial pH value affected on the uptake of Fe^{3+}, Al^{3+} and Cr^{3+} using **Cell-FoNPs** has been tested in pH range 1-5, before the precipitation limits, asshown in Fig.3. The capacity of Fe^{3+}, Al^{3+} and Cr^{3+}adsorption gradually increases by increasing pH value. The adsorption is occurs through coordination between the active sites present 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 Fe^{3+}, Al^{3+} and Cr^{3+} at lower pH

3.3. The thermodynamic studies

The parameters of thermodynamic such as enthalpy (ΔH°) and free energy (ΔG^{o}), entropy (ΔS°) of the adsorption process of **Fe^{3+}, Al^{3+} and Cr^{3+}**by **Cell-FoNPs**, as chelating Fibers. The parameters 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).

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

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

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 ($\Delta S^{o}_{ads} /R$) 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 show* decreasing 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.

3.4. Kinetic studies

Fig. 7 shows the kinetics of the adsorption of the studied metal ions Fe^{3+}, Al^{3+} and Cr^{3+} by **Cell-FoNPs**. Inspection of the uptake–time curves show that the maximum uptake follows the order $Fe^{3+}>Al^{3+}>Cr^{3+}$ at all-time intervals. The kinetic curve for Fe^{3+} ions showed that the adsorption was initially rapid and reached equilibrium after approximately 100 min. Al^{3+}ions adsorption reached equilibrium in 100 min, and remained constant until the end of the experiment. Cr^{3+} ions adsorption showed the slowest kinetic profile of all, reaching equilibrium at approximately 110 min.

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

$$1/qt= \; k1/q_et + 1/qe \qquad (6)$$

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

Where q_t (mg.g^{-1}) and q_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 adsorptionrate 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 favored when the value of correlation coefficient is close to unity and also compare

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

Based on the obtained correlation coefficients (R^2), the pseudo-second-order equation is the model that furthered the best fit for the experimental kinetic data, suggesting chemical sorption as the rate-limiting step of the adsorption mechanism and no involvement of a mass transfer in solution.

3.5. Adsorption isotherms

The obtaining results were studied with both Freundlich and Langmuir isotherm models and all the parameters have been shown in Table (4). As shown, model of Langmuir showed the best fit for the obtained data from the correlation coefficient values. The maximum adsorption capacities for Fe^{3+}, Al^{3+} and Cr^{3+} with **Cell-FoNPs** are 77, 61 and 50 (mg/g) respectively.

The adsorption process suitability could be 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 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-FoNPs**under study as adsorbents for metals under study from aqueous solution.

3.6. Fibers reusability

From examining the reusing of modified cellulose, five cycles of adsorption-desorptionhave been performed under optimum conditions and the results were presented in Table 5. It is shown that the uptake efficiency of the **Cell-FoNPs** modified cellulose didn't show a significant decrease. After the fifth cycle, the modified cellulose maintains about 87% of its original efficiency. According to these results, it is expected that **Cell-FoNPs** fibers would be a promising adsorbent for fast removal of Fe^{3+}, Al^{3+} and $Cr^{3+}$from water

3.7. *Analytical applications of the present method*

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

3.7.2 *Statistical* evaluation for Fe^{3+}, Al^{3+} and Cr^{3+} in natural water samples collected from several locations of El-Dakahlia Governorate at 26th June 2014 after pre-concentration by (**Cell-FoNPs**) 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), its 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 with relative high value of Sinbelawien waste water station (d) Table (7).

The F-test also shows that all water samples are not subjected to random errors

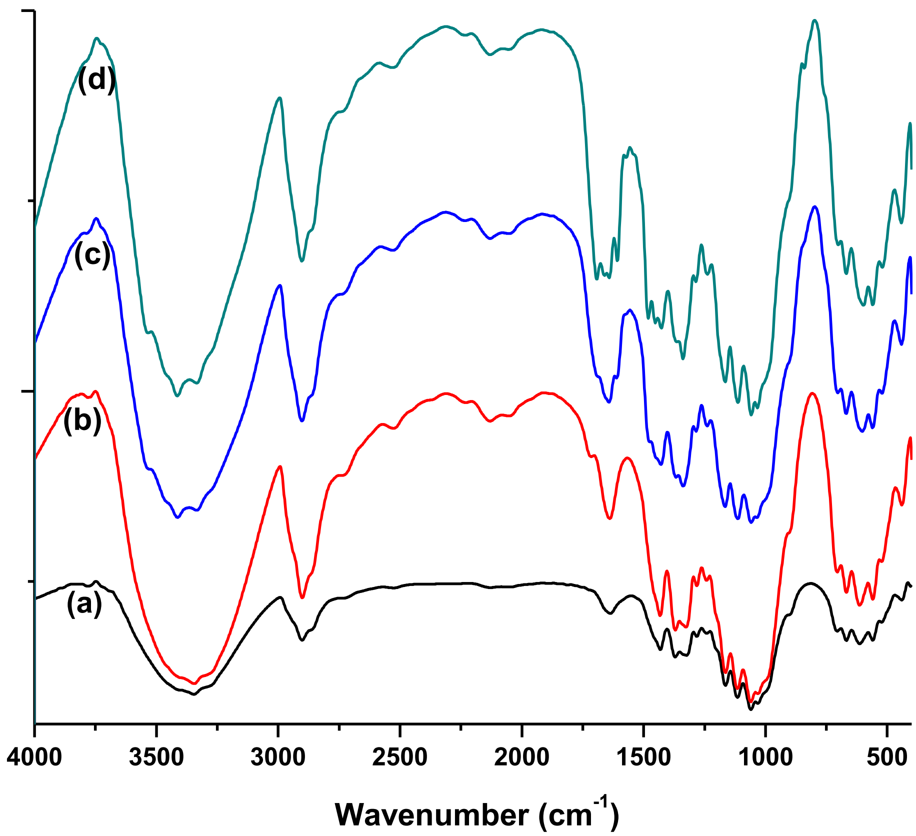
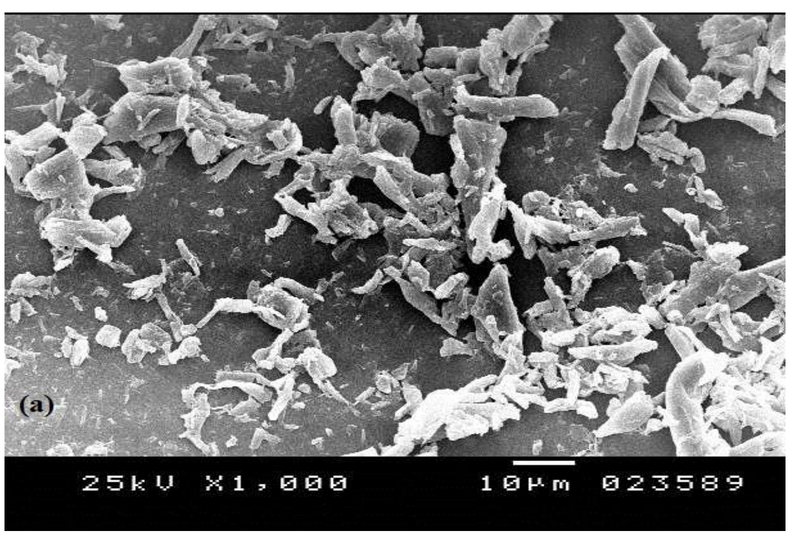


Fig. 1 IR spectra of (a) cellulose, (b) DAC, (c) folic acid and (d) Cell-FoNPs.



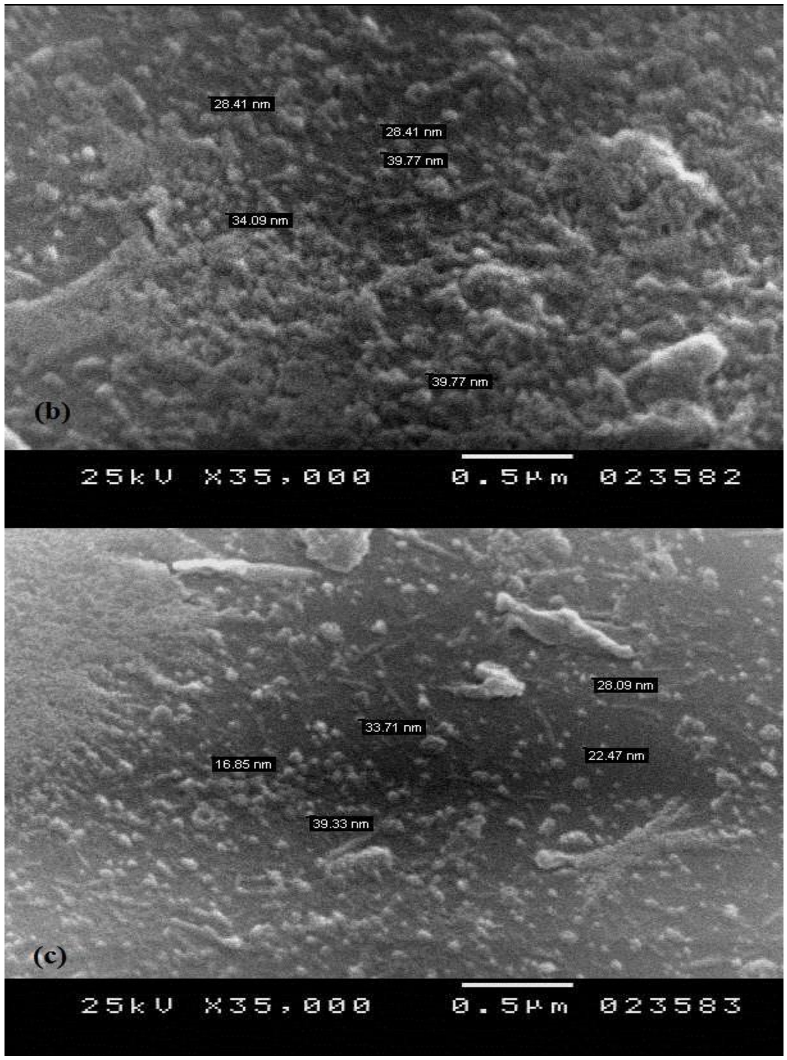


Fig. 2SEMsimage of (a) cellulose, (b) DAC, (c) Cell-FoNPs.

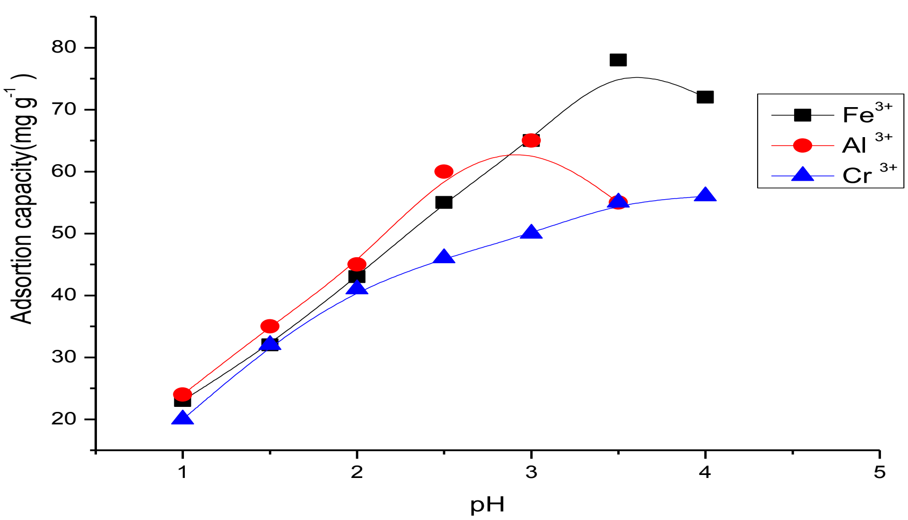


Fig. 3.Effect of pH on the uptake of [**Fe^{3+}, Al^{3+} and Cr^{3+}**] ions by **Cell-FoNPs** (30 ml (100 mg/L) , adsorbent 0,034 g, contact time 3 h, shaking rate 150 rpm, 25^{0}C).

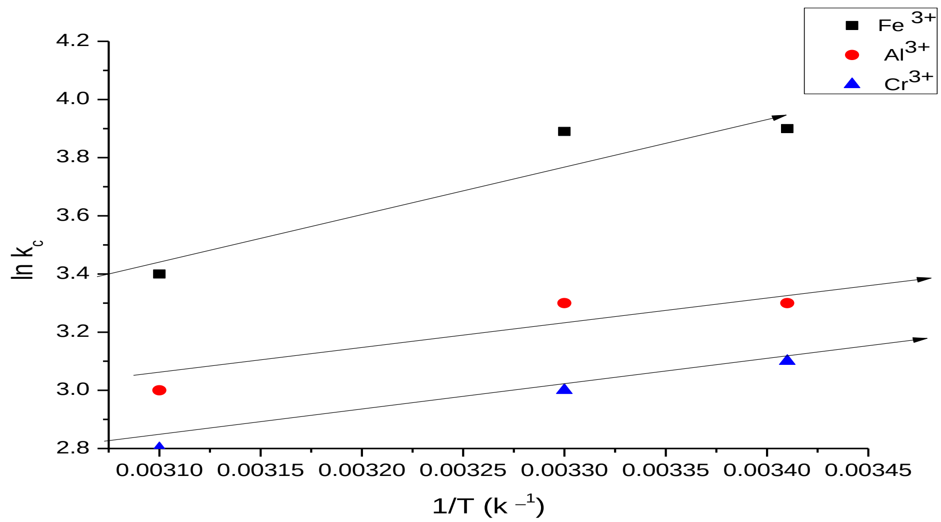


Fig. 4 .Plot of lnK_C as a function of reciprocal of absolute temperature (1/T) for the adsorption of **Fe^{3+},Al^{3+} and Cr^{3+}**

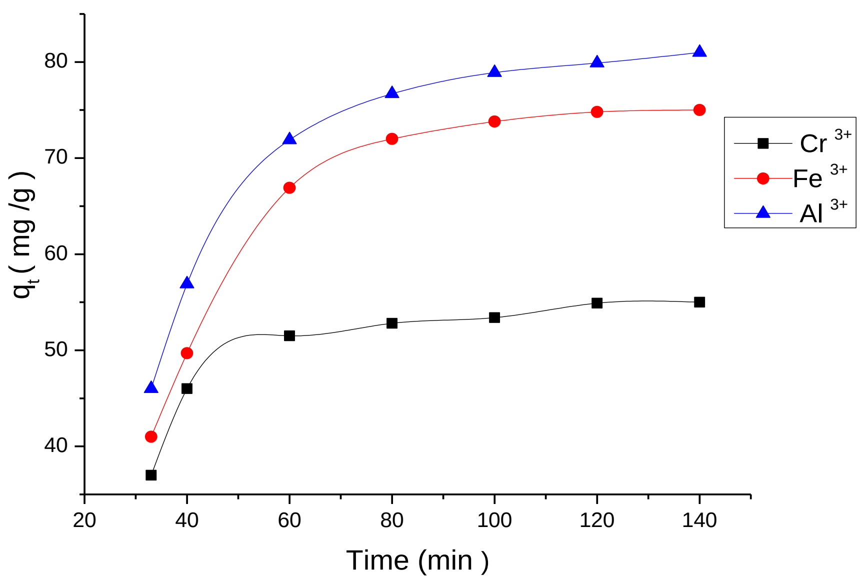


Fig. 5. Effect of contact time on the uptake of (**Fe^{3+}, Al^{3+} and Cr^{3+}**) ions by **Cell-FoNPs** (40 ml(150 mg/L), adsorbent. 0,04 g, pH 3-5, shaking rate 150 rpm, 25^{o}C).

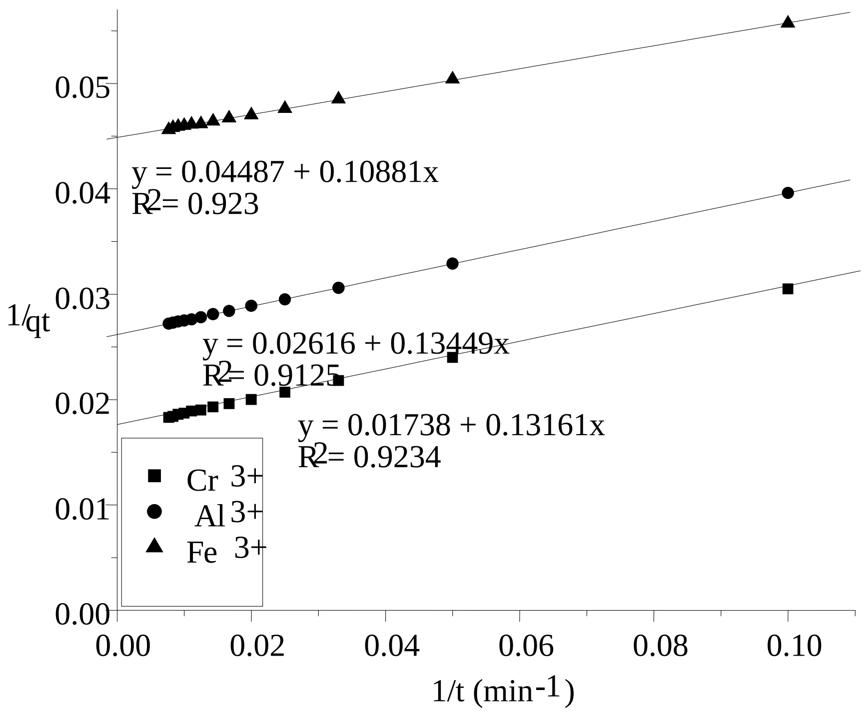


Fig. 6.pseudo – first kinetics of the uptake of (**Fe^{3+}, Al^{3+} and Cr^{3+}**) on **Cell-FoNPs**

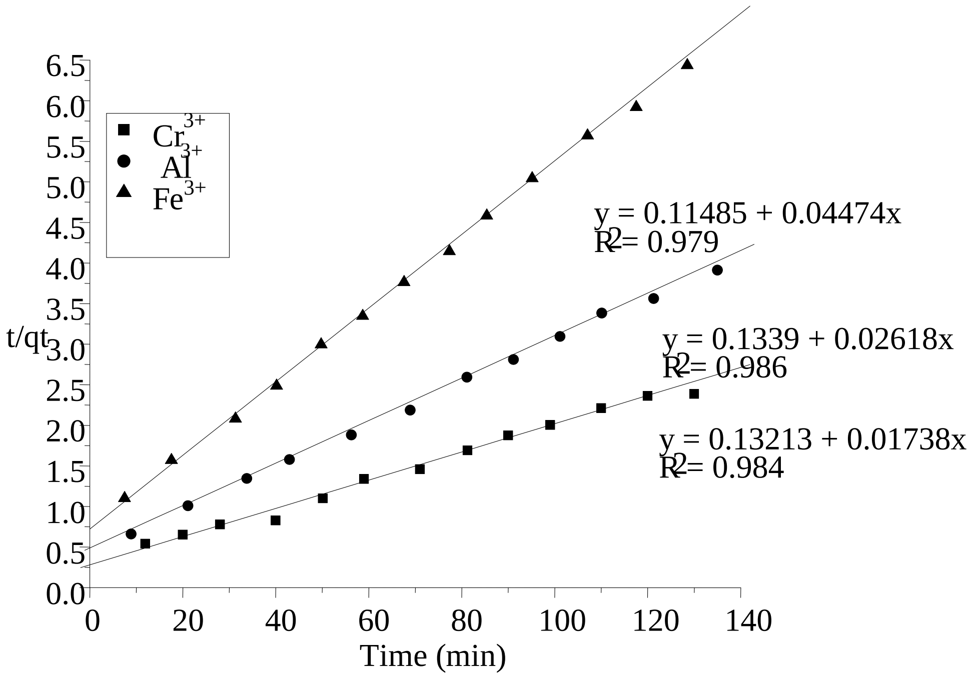


Fig. 7.pseudo second kinetics of the uptake of (**Fe^{3+}, Al^{3+} and Cr^{3+}**) on**Cell-FoNPs**

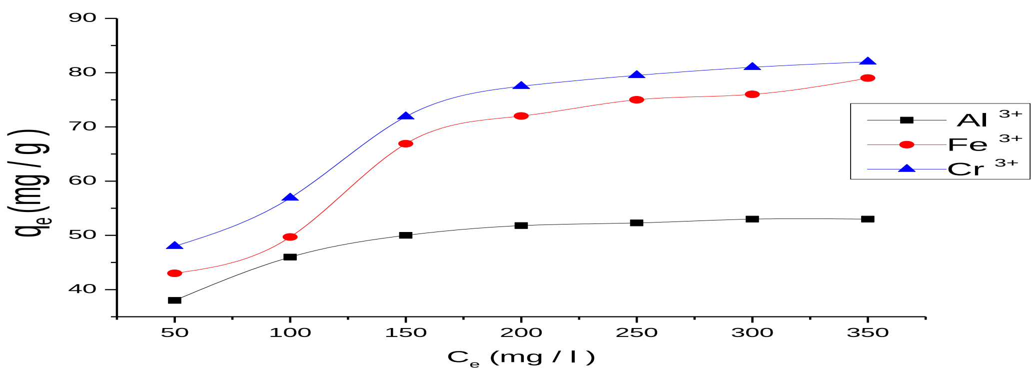


Fig.8. Adsorption isotherms of **Fe^{3+}, Al^{3+} and Cr^{3+}** ions by **Cell-FoNPs** (initial concentration (10-350) mg/L, adsorbent 0.04g pH 3-5, shaking rate 150 rpm, 25◦C).

Table 1 Elemental analysis of cotton, C-EDA, and C-TU.

Fibers	C(%)	H(%)	N(%)
cellulose	43.2	6.01	--------
Cell-FoNPs	50.1	9.5	19.5

Table2 : Thermodynamic parameters for the adsorption of **Fe^{3+},Al^{3+} and Cr^{3+}**by **Cell-FoNPs**

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	-32.098	-51.654

Fe-Cell-FoNPs	313	288	274	19.765	19.098	13.987		
Al-Cell-FoNPs	253	231	199	12.87	12.46	11.980	-29.573	-42.985
Cr-Cell-FoNPs	179	160	149	10.98	11.5	9.4	-24.623	-33.823

Table 3. Kinetic parameters for adsorption of (**Fe^{3+}, Al^{3+} and Cr^{3+}**) by **Cell-FoNPs**.

Fibers	First-order model		
	k_1 (min^{-1})	q_{e1}(mg/g)	R^2
Fe-Cell-FoNPs	7.2	77±3	0.9117
Al-Cell-FoNPs	6.3	63±2	0.9337
Cr-Cell-FoNPs	3.3	55±4	0.9227
Fibers	**Second-order model**		
	k_2 (g/(mg min))	q_{e2} (mg/g)	R^2
Fe-Cell-FoNPs	4.1×10^{-3}	84± 2	0.9987
Al-Cell-FoNPs	3.3×10^{-3}	63± 3	0.9988
Cr-Cell-FoNPs	1.7×10^{-3}	50± 2	0.995

Table .4.Physico chemical adsorption of **Fe^{3+}, Al^{3+} and Cr^{3+}** ions by **Cell-FoNPs**

Fibers	Langmuir isotherm constants			
	K_L(L/g)	q_m(mg/g)	R^2	R_L
Fe-Cell-FoNPs	$18x10^{-2}$	78	0.996	(0.012-0.541)
Al-Cell-FoNPs	$15x10^{-2}$	62	0.97	(0.013-0.451)
Cr-Cell-FoNPs	$13x10^{-2}$	51	0.988	(0.015-0.451)
Fibers	**Freundlich isotherm constants**			
	K_F	n	R^2	
Fe-Cell-FoNPs	13.452	3.2	0.8988	
Al-Cell-FoNPs	11.385	2.5	0.9187	
Cr-Cell-FoNPs	7.772	3.3	0.9212	

Table.5: Repeated adsorption of **Fe^{3+}, Al^{3+} and Cr^{3+}**ions by **Cell-FoNPs**(initial concentration 100 mg/L, **Cell-FoNPs** 0.02 g, pH3-5.0, contact time 3h, shaking rate 150 rpm, 25◦C)

Cycle number	Recovery(%) by **Cell-FoNPs**		
	Fe^{3+}	Al^{3+}	Cr^{3+}
1	100	100	100
2	95.4	98.7	96.3
3	94.4	97.6	95.2
4	93.2	93.3	94.4

5	87.8	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
Intake of Sinbelawin water station(a)	30.9	7.77	165	5.7	303
Thickener of Sinbelawin water station(d)	31	6.9	124	1.3	412
Karkera well (c)	25	7.98	214	3.9	772
Sinbelawin waste water station(d)	29.8	7.4	146	2	456
Intake of Hagayza water station(a)	31	7.69	158	5.4	317
El Mansoura city (b)	31.2	7.25	120	8.3	316

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**			
	Cr^{3+}						
Thickener of Sinbelawin water station(d), El-Dakahlia Governorate	**0.29**	**0.03**	**0.25**	**0.025**	**0.027**	**2.29**	**1.44**
Karkera well (c), El-Dakahlia Governorate	**0.10**	**0.01**	**0.13**	**0.013**	**0.032**	**1.5**	**1.69**
Sinbelawin waste water station(d), El-Dakahlia Governorate	**0.45**	**0.04**	**0.43**	**0.038**	**0.039**	**0.83**	**1.10**
Intake of Hagayza water station, (a) El-Dakahlia Governorate	**0.16**	**0.015**	**0.14**	**0.013**	**0.014**	**2.2**	**1.33**
El Mansoura city (b), El-Dakahlia Governorate	**0.21**	**0.02**	**0.19**	**0.019**	**0.0195**	**0.83**	**1.10**
Al^{3+}							
Intake of Sinbelawin water station(a)	**1.8**	**0.15**	**1.9**	**0.14**	**0.145**	**1.11**	**1.14**
Thickener of Sinbelawin water station(d)	**3.2**	**0.2**	**3.21**	**0.07**	**0.176**	**0.09**	**4.16**
Karkera well (c)	**1.0**	**0.09**	**0.98**	**0.08**	**0.083**	**0.37**	**1.26**
Sinbelawin waste water station(d)	**19.2**	**0.6**	**20.0**	**0.23**	**0.45**	**2.8**	**6.8**
Intake of Hagayza water station(a)	**2.5**	**0.19**	**2.3**	**0.17**	**0.18**	**1.76**	**1.24**
El Mansoura city (b)	**2.5**	**0.19**	**2.3**	**0.17**	**0.18**	**1.76**	**1.24**
Fe3+							
Intake of Sinbelawin water station(a)	**0.39**	**0.08**	**0.41**	**0.07**	**0.075**	**1.27**	**1.30**
Thickener of Sinbelawin water station(d)	**0.42**	**0.075**	**0.44**	**0.07**	**0.072**	**1.10**	**1.14**
Karkera well (c)	**0.39**	**0.074**	**0.40**	**0.065**	**0.069**	**1.16**	**1.29**
Intake of Hagayza water station(a)	**0.37**	**0.08**	**0.39**	**0.07**	**0.075**	**1.27**	**1.3**
El Mansoura city (b)	**0.38**	**0.082**	**0.41**	**0.075**	**0.078**	**1.02**	**1.19**

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

$^{**}\left|t\right|_2 = (\overline{X}_1 - \overline{X}_2) S_P \sqrt{1/n_1 + 1/n_2}$ **, 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)

4. Conclusions

In this work, novel modified cellulose (**Cell-FoNPs**) 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-FoNPs** 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 mono layer adsorption of metal ions.

The present method was applied to real samples taken from different water stations around El-Dakahlia Governorate and compared with the standard solvent extraction method. The obtained results were satisfied and agreed with the standard solvent extraction method.

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