

Article

Adsorption of heavy metals (cadmium, chrome and copper) on grafted cellulose: Establishment of kinetic models

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Abstract

Chemical modification by grafting cellulose in the biological field produces a cellulosic material with improved absorption. Acrylamide was grafted onto cellulose fibers using a free radical process initiated by a redox initiator system: the ceric ion (ceric ammonium nitrate). For the grafted cellulose, it is noted that the optimum pH is equal to 5 because of the presence of amide groups. Also, the adsorption capacity of chromium is greater than that of the grafted cellulose ($Q_e = 14.2 \text{ mg / g}$) et almost triple for copper and cadmium. The effect of concentration on retention is extremely important for chromium and cadmium, which have the retention of around 18/20 mg / g. The increase in ionic strength leads to a decrease in the amount of adsorbed metal ions resulting from the competition between these metal ions and salt ions. The results of a kinetic study for all the heavy metals indicated that the retention is extremely fast; it is almost instantaneous. Linear regressions shown that kinetics are controlled by the pseudo-second-order model. Thus, the chrome is controlled by the pseudo-first-order model. This is clearly confirmed by the values of the correlation factors corresponding to each model. The adsorption of isotherms in the cadmium and chromium concentrations chosen for initial experimental data were interpreted by the Redlich-Peterson and Langmuir models for unbleached and grafted cellulose. For copper, the Freundlich model best described the data of adsorption isotherms on unbleached cellulose, and the Redlich-Peterson and Langmuir models were the most appropriate for the retention of copper for the grafted cellulose.

Keywords cellulose; grafting; copolymerisation; acrylamide; absorption capacity; kinetics; adsorption isotherms; heavy metals; cadmium; chromium; copper.

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1 Introduction

Environmental protection is a major concern of our society, prompting us to encourage the development of processes for improving pollution control methods, while focusing on reducing pollution sources (Dubey et al., 2015; Meravi and Prajapati, 2013, 2014). Water is the most vital natural source and, whether it is intended for human consumption, irrigation or simply discarded in the wild. It has become a major problem and a huge concern for and local authorities, and national and international organizations. It is imperative to check its quantitative and qualitative use.

The massive and diversified discharge of industrial wastewater containing toxic residues into the natural environment is threatening the balance of the natural environment and ecosystems, especially for humans. This situation has made it imperative to save our lives by improving pollution control techniques and developing new processes in order to meet our needs, to preserve our ecosystem for future generations and to comply with international standards, which are characterized by increasingly restrictive water regulations.

A variety of techniques have been used for the removal of certain chemical pollutants from industrial or domestic effluents. These techniques differ widely; they include adsorption, electrolysis, flotation, precipitation, ion exchange, liquid-liquid extraction and membrane filtration.

However, the absorbency of some materials has always been preferred for their ability to elute micro-pollutants. Less expensive materials for lead, cadmium, chrome, copper and arsenic removal from water include algae (Al-Degs et al., 2006; Klimmek et al., 2001), carbon cloth (Kadirvelu et al., 2000), peat (Ho et al., 2001), agricultural by-products (Wafwoyo, 1999), lignin blast furnace slag (Srivastava et al., 1994), red mud (Altundogan et al., 2002), biomaterials (Minamisawa et al., 2004), bagasse fly ash (Gupta and Trifunac, 1993), iron oxide coated treated sand (Gupta et al., 2005) and mangrove rhizomes in wetlands (Chowdhury et al., 2017). Low cost adsorbents for water remediation have also been reviewed (Rodavic et al., 2001). For crude fibrous polymers, the elimination rate is as low as 30% to 35%. Thus, new opportunities for natural polymers have benefitted from the provision of original materials, referred to as generic biopolymers, because they are emerging materials with unique and unexplored properties, and offer interesting possibilities for use in new applications (Babu et al., 2013).

These materials are in the form of cross-linked polymer networks and have the ability to absorb and retain a substantial amount of liquid. However, their major disadvantage is the weakness of their mechanical characteristics in the inflated state. Unlike conventional biopolymers, fibrous polymers exhibit excellent mechanical behavior due to a relatively high degree of orientation, namely 70%. Among the natural fibers, it is preferably used as an absorbent material in biomedical and hygienic applications. In the last few years, the rapid development of cost-effective paper-based technologies has been registered in the field (Genovese et al., 2018).

In a standardized atmosphere, cellulose in various physical forms can absorb up to 10% moisture. In a liquid medium, it has a great absorbency, thanks to its high capillarity. However, if the cellulose has a high affinity for water (hydrophilic), it retains little liquid in its internal network. The role of the capillary system of cellulosic products in the absorption of liquids is known. This capillary system can be modified in different ways such as:

- Acting on the fiber module to increase the effective pore diameter.
- Microfibrillation of the fiber to increase the specific surface of the adsorbent material, resistance to microbiological attack and thermal degradation (Gurdag et al, 2013), and water and oil repellency (Bayer et al, 2011; Paul et al., 2016).
- Bridging action to prevent pore destruction

Polymer grafting can achieve sufficient swelling and increase the number of adsorbent sites.

To understand the concept of grafting, it should be known that all fibrous supports can be activated and modified imperceptibly to acquire properties that are revealed only in use. In the general scheme, the acquired properties will be due to the chemical nature of the monomers used; their intensity will be defined, as a first approximation, by the grafting rate. Activated sites are created on the polymeric material by breaking covalent bonds. This technique customizes the properties, making them unlike existing materials (Kaewtatip and, Tanrattanakul, 2008). Cellulose is the constituent that provides protection and support in plant organisms (Sarkar et al., 2009). It is the most abundant organic substance in nature. Indeed, it is estimated that a tree produces about 10 grams of cellulose per day. It is a homopolysaccharide composed of β -D-glucopyranose units linked together by a glycosidic bond β - (1- 4) (substitution of a hydroxyl group (OH) monovalent radical) of the hemiacetal of a sugar with a hydroxyl group of an alcohol of another sugar (Stannett et al., 1973; Stage 2002).

The origin of the specific properties of fibrous polymers is in the macromolecular structure. That enables us to modify the polymer and improve its properties. There are several ways to do this. The most used are mixing (blending), grafting and reticulation (Bhattacharyya and Misra, 2004). Several specific grafting procedures have been introduced (Hebeish and Guthrie, 1981; Garnett and Jankiewicz, 1981; Stannett and Williams, 1976). Grafted cellulose copolymers are developed for a wide variety of cellulose properties, including: resistance to microbial degradation, abrasion, ion exchange, acid resistance, adsorption, wet fastness and membership (Stannett and Williams, 1976; Stannett et al., 1973; Rowell and Young, 1974). The grafting of a monomer onto a polymer to obtain a graft copolymer leads to the creation of active centers on the boot polymer. These sites can then be used as polymer initiators

The grafting technique makes it possible to modify the polymers effectively. It has many applications in various fields of advanced technology, such as biology, membrane synthesis and surgery. Many studies have been devoted to membrane synthesis (Bhattacharyya and Maldas, 1984). This grafting process has facilitated an increase in the water permeability of cellulose acetate membranes during the desalination processes. It increases ion exchange (strong and weak ions) and is applied in various separation techniques for purification, extraction, the treatment of industrial effluents, nuclear, pharmaceutical and food (Sun et al., 2019; Ceresa, 1962), and a cellulose acetate membrane grafted with polystyrene (McDowall et al., 1984). The use of membranes prepared by grafting polystyrene onto a porous PolyVinylidene Fluoride (PVDF) to effect the separation of ethanol-water mixtures by pervaporation have been reported (Simionescu and Macoveanu, 1977).

The graft polymers can be used to separate one or more substances from a complex mixture selectively, through ionic bonds or by electrostatic forces. It is therefore possible to separate species by covalent chemical bonds. The undesirable species supported on the polymer can be recovered by a simple reaction, for example by a simple variation of pH. Heavy metals are hazardous to the environment and human health and are highly toxic when present in industrial effluents (Hachache, 2005). Currently, their separation is the subject of very serious studies.

In this study the aim was to show the importance of the chemical grafting of cellulosic materials to obtain a material with absorption and the improved retention of inorganic pollutants, such as chromium, copper and cadmium, and the influence of certain physical and chemical parameters on the adsorption capacity of our biomaterial. Moreover, we tested the two materials under real conditions after physicochemical characterisation of the oily water (HaoudBerkaoui - Hassi-messaoud-algeria).

2 Materials and Methods

2.1 Adsorbents

Cellulose is a linear homopolysaccharide composed of a chain of D-glucopyranose units that have free OHs at positions 2, 3 and 6, and which are linked together by P- (1-4) glycosidic bonds (Ulbricht, 2006). The principal unit is cellobiose, which consists of two glucoses arranged to 1800 units relative to the other, giving the molecule its linear character.

2.2 Grafted cellulose

In this work, we grafted and copolymerized an acrylic derivative 'acrylamide' onto cellulose, using ceric ions as the initiation system (Ozacar and Sengil, 2003; Fakhre and Ibrahim, 2018). A known amount of cellulose was placed in a necked flask, providing an outlet for the wading nitrogen. An appropriate volume of monomer was then added and, after the contact time, an amount of ammonium ceric nitrate solution in HNO_3 .

After three hours of stirring, the grafted cellulose was filtered, washed and dried. As a redox system, we used ceric ammonium nitrate (IV), $[\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6]$ (Sheela et al.; 2016; Gürdağ et al., 1999; Aliouche and Djelali, 2005) and we obtained a graft polymer (Fig. 1).

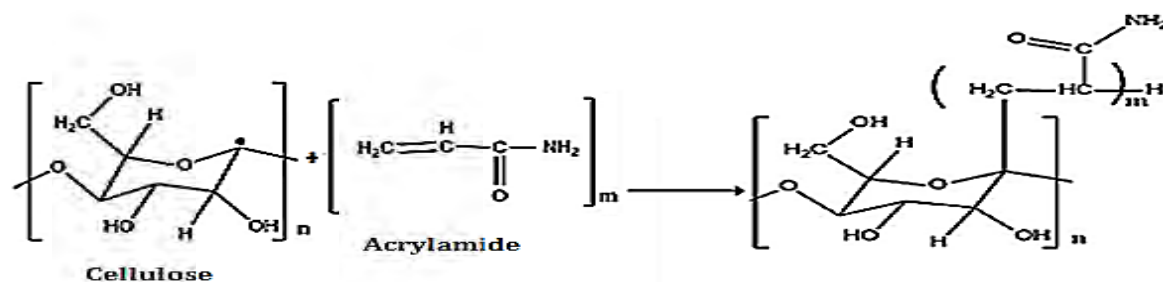


Fig. 1 The chemical structure of grafted cellulose.

3 Results and Discussion

3.1 The optimized grafting rate

The optimized grafting rate adopted was approximately equal to 30% of the total weight of the material. Wetting or swelling was tested with three alcohols, with a generally accepted temperature of 30 °C. This rate gave us a fairly condensed material texture, which swelled to better moisten and consequently better adsorb by increasing the number of active sites and inhibiting adsorption with chemicals used for grafting; another advantage was a controlled increase in the volume of the material when used in fixed bed.

3.2 Characterization of raw materials and graft

3.2.1 Fourier Transformed Infrared Ray (FTIR)-spectroscopic analysis

The grafting results were confirmed by infrared analysis, using the pelletizing technique in "Potassium bromide "KBr". The measurements were also confirmed by spectrophotometry (Perkin Elmer 225). The results were confirmed by characteristic bands of the monomers observed for our samples (Fig. 2).

- Interpretation of the IR spectrum of pure cellulose

Peaks and bands (cm^{-1})	Groupings
3337.01	Valence vibration of the hydroxyl group O-H.
22895.88	Valence vibration corresponding to C-H, CH ₂

- Interpretation of the IR spectrum of grafted cellulose

Peaks and bands (cm^{-1})	Groupings
3419.8	Valence vibration of the hydroxyl group O-H.
2848.56	Valence vibration corresponding to C-H, CH ₂
1800.56	Valence vibration of the bond (-C = O) of the amide carbonyl

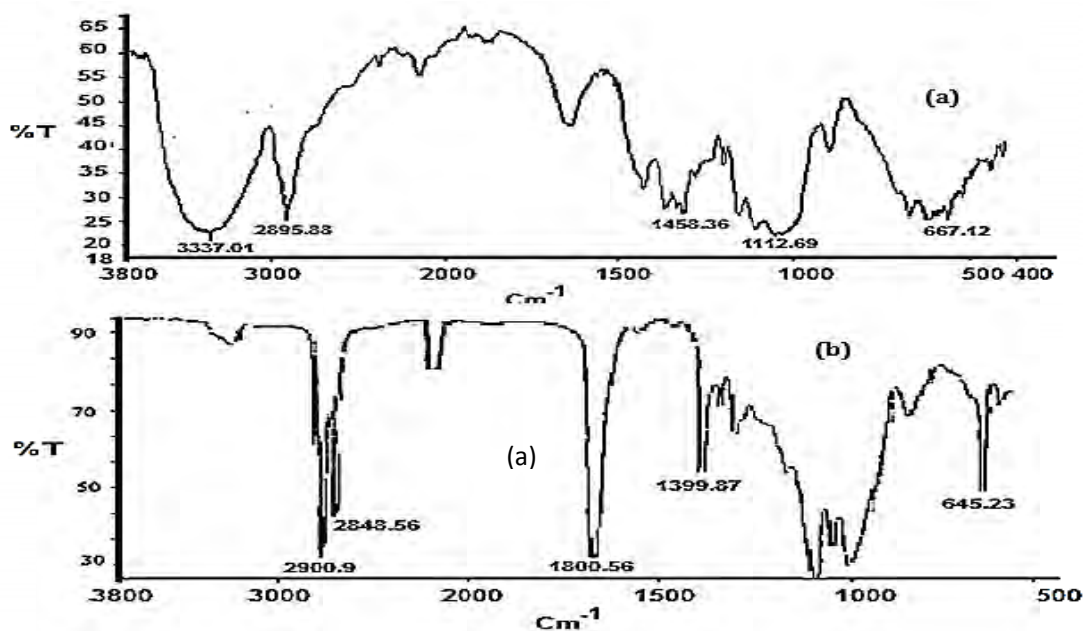


Fig. 2 FTIR spectrum of pure cellulose (a) and grafted cellulose (b).

Vibrations appearing in the spectrum of the grafted cellulose in the bands 1800.56 2848.56 and reveal the bond (-C = O) of the amide carbonyl and the bond (= CN) of the primary amides resulting from grafting the acrylamide onto the cellulose.

3.2.2 The physicochemical characteristics of the samples

Physicochemical analyses were carried out on samples with decantable suspended solids and without extraction of the oily phase of the wastewater after the sedimentation and extraction of hydrocarbons (Table 1).

Table 1 The physicochemical characteristics of the sample before and after treatment with and without extraction and without MES for unbleached cellulose.

Parameters	Units	Before treatment	After treatment by grafted cellulose					
			Without extraction	%	With settleable solids and extraction	%	Without settleable solids and extraction	%
Température	C°	23			4.21		30	
pH		3,42	5,88		6,11		6,62	
MY	Mg/l	1103.2	678.145	38,52	412,324	62,63	/	
COD	Mg/l	34800	13393	61,51	3487	89,98	1120	96,78
TOC	Mg/l	1299	689	46,96	108	91,69	Absence	100
hydrocarbons	Mg/l	33,79	8.58	74,61	Absence	100	Absence	100
cyanide	Mg/l	0.704	0,231	67,19	0,196	72,16	0.151	78,55
Dissolve salts	Mg/l	937,12	155.78	83,38	76.39	91,85	48,16	94,86
phosphates	Mg/l	6,52	2,12	67,48	1,02	84,36	0,468	92,82
nitrates	Mg/l	67,33	22,26	66,94	13,48	79,98	9,12	86,45
nitrites	Mg/l	1,03	0,654	38,39	0,183	81,99	0,081	91,86
Turbidity	NTU	721	93,43	87,04	72,69	89,92	29,58	95,90
Conductivity	ms/cm	189.5	165,3	12,28	132,9	29,87	115,4	0,391

Table 2 The physicochemical characteristics of the sample before and after treatment without and with extraction and without MES for grafted cellulose

Paramètres	Units	Before treatment	After treatment of unbleached cellulose					
			Without extraction	%	With settleable solids and extraction	%	Without settleable solids and extraction	%
Température	C°	21	20					
pH		3,42	5,38		5,85		6,06	
MY	Mg/l	1103.2	855,212	22,48	568.131	48,50	/	/
COD		34800	18420	47,07	5562	84,02	1370	96,06
TOC		1299	846	34,87	194	85,07	Absence	100
hydrocarbons		33,79	11.23	66,77	Absence	100	Absence	100
cyanide		0.704	0,415	41,05	0,23	67,33	0.167	76,29
Dissolve salts		937,12	170.81	81,77	83.38	91,10	54,79	97,15
phosphates		6,52	4,32	33,74	2,46	62,27	0,956	85,34
nitrates		67,33	32,45	51,80	16,54	75,43	10,45	84,48
nitrites		1,03	0,765	25,73	0,357	65,33	0,212	79,41
Turbidité	NTU	721	106.9	85,17	83.8	88,38	39,4	94,53
Conductivité	ms/cm	189.5	177,2	6,49	145,1	23,43	123,8	34,67

3.3 Heavy metal concentration before and after treatment of raw water

The following tables show the heavy metal content before and after the treatment of unbleached cellulose, and grafted onto the raw water without treatment and after treatment, with extraction of the oily phase and without settleable solids.

Table 3 and 4 show that our raw water sample was loaded with heavy metals. After the removal of the oily phase (hydrocarbons) and decantable suspended solids, we obtained a yield of elimination of the pollution indicators that was better than the efficiency of the adsorption obtained before extraction and with MES. This was valid for unbleached cellulose, which demonstrates the need for pigments' preliminary treatments (oiling, decantation) before adsorption, which can make our adsorbents more efficient and profitable.

Table 3 the heavy metals concentration before and after treatment on unbleached cellulose with and without extraction and without settleable solids.

Heavy metals (mg/l)	Before treatment	After treatment of pure cellulose					
		Without extraction	%	With settleable solids and extraction	%	Without settleable solids and extraction	%
Mn	75.821	23.920	68,45	14.5	80,87	2,256	97,02
Fe	245.80	90.99	62,98	20.834	91,52	8,564	96,52
Zn	1.256	0.756	39,81	0.601	52,15	0,076	93,95
Cu	1.947	0.885	54,51	0.118	93,94	0.025	98,72
Pb	4.844	1.624	66,47	1.401	71,08	0.258	94,67
Cd	2.776	0.785	71,72	0.383	86,20	0.102	96,33
Cr	1.923	0.682	64,53	0.429	77,69	0.095	95,06
Ni	0.275	0.165	40,00	0.139	49,45	0,112	59,27

Table 4 the heavy metals concentration before and after treatment on grafted cellulose with and without extraction and without settleable solids.

Heavy metals (mg/l)	Before treatment	After treatment of grafted unbleached cellulose					
		Without extraction		With settleable solids and extraction		With settleable solids and extraction	
			%		%		%
Mn	75.821	19.451	74,35	10.527	82,84	1,003	98,68
Fe	245.80	97.99	60,13	17,368	92,93	6,932	97,18
Zn	1.256	0.451	64,09	0.290	76,91	0,012	99,04
Cu	1.947	0.792	59,32	0.093	95,22	0.0067	99,66
Pb	4.844	1.784	63,17	1.236	74,48	0.236	95,13
Cd	2.776	0.626	77,45	0.124	95,53	0.087	96,86
Cr	1.923	0.579	69,89	0.381	80,02	0.068	96,46
Ni	0.275	0.091	66,90	0.024	91,64	0,002	99,27

3.4 Analysis of the morphology by electron microscopy

The morphological characterization of the cellulose was carried out on a SEM ‘Type Quanta 650’. We observed the changes induced by the grafting process on the fiber morphology. The external morphology of the grafted and unbleached fibres can be seen in Fig. 3.

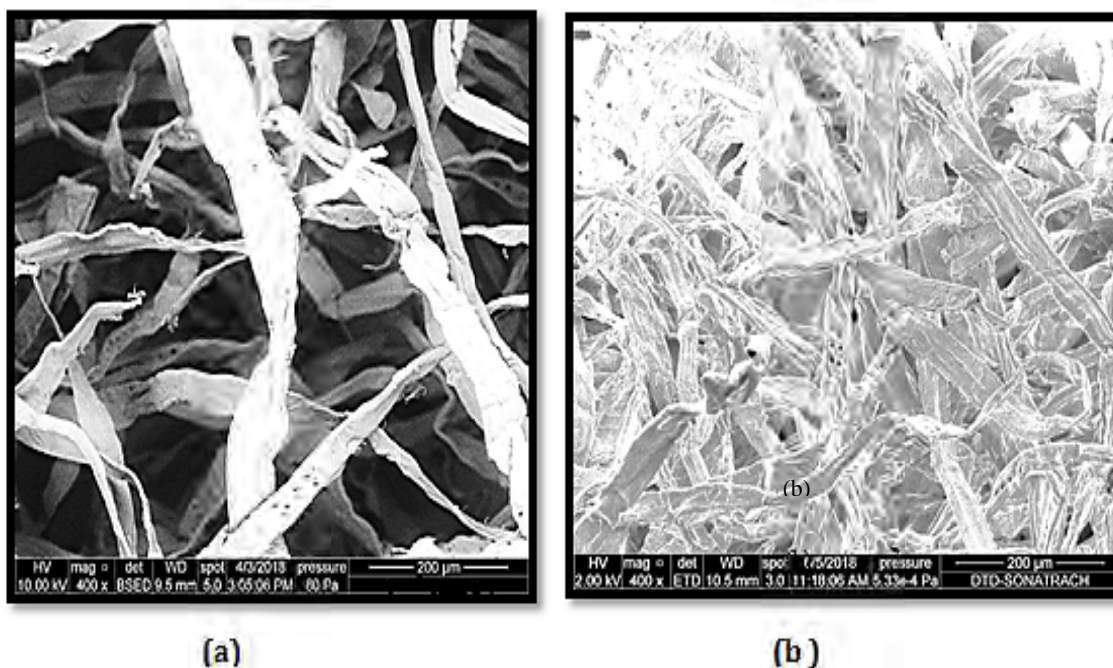


Fig. 3 Micrographics of pure cellulose fibers (a) and grafted cellulose fibers (b).

This microscopic analysis enabled us to observe how the surface condition was affected by the grafting, showing a surface composed of fibrils, characteristic of the cellulose fibers, because it showed the condensation of the grafted cellulose. Thus increasing the available surface area aids adsorption. Therefore, an increase in the active sites’ porosity is certainly variable with a slight swelling permeable, allowing optimum permeability without a real increase in the volume used in the case in which the adsorption is in a fixed bed.

3.5 Operating conditions

All the chemicals were of an analytical grade and used without further treatment. De-ionized water was used in all the experiments. $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and $\text{K}_2\text{Cr}_2\text{O}_7$ were used to prepare the stock metal solutions.

To study the retention of metallic ions by adsorption on cellulose, the experimental work plan was based on: (1) study of the influence of physicochemical parameters (contact time, pH, the initial concentration and ionic strength of the retention process of copper and cadmium by varying one parameter at a time); (2) the determination of the nature of the adsorption isotherm; (3) determination of the adsorption kinetics; (4) the kinetics of adsorption was carried out by repeating the equilibrium study described previously for differing durations of contact.

The knowledge of equilibrium time was necessary for the establishment of kinetic adsorption models.

3.6 Effect of physicochemical parameters

3.6.1 The effect of contact time on the retention of Cd^{2+} , Cu^{2+} , Cr^{6+}

The results are expressed as a curve, giving the amount (mg) of copper, cadmium and chromium adsorbed per gram of support (Q_e mg / g) versus time (Fig. 4).

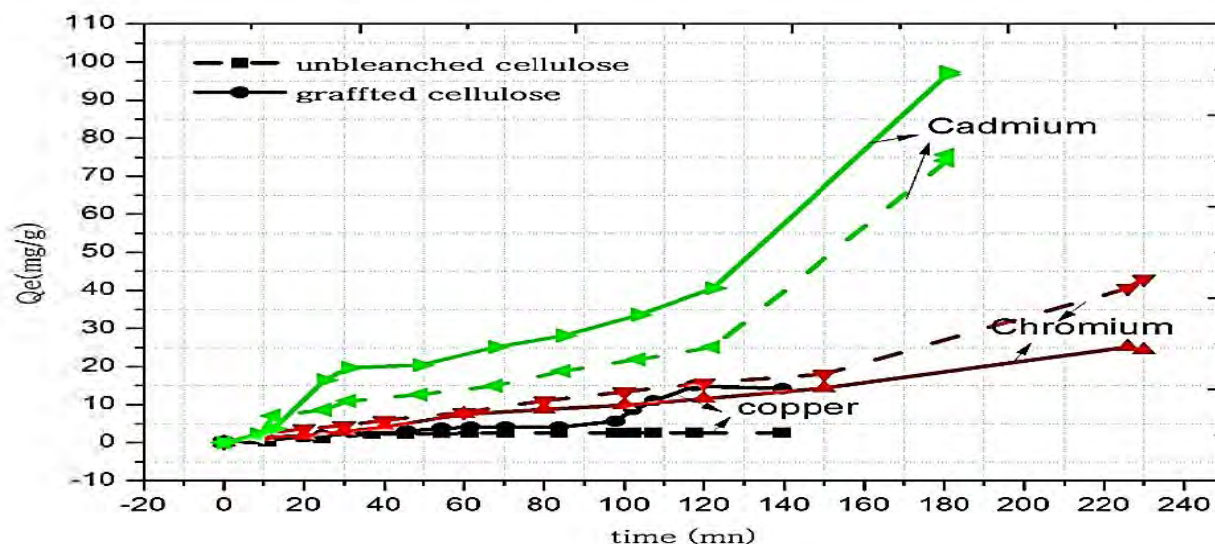


Fig. 4 The effect of contact time on retention copper ions: $C_0 = 20$ mg / l, $T^\circ\text{C} = 20 \pm 2$, $V_{\text{agitation}} = 350$ rpm, $\text{pH} = 5.33$.

We can consider, based on the results that the retention of ions consists of two distinct stages. The adsorption is initially rapid and transient, then it becomes stable when the steady state is reached, but at differing times (60 minutes for copper, 120 minutes for cadmium and 150 minutes for chromium). The time factor has an immense influence on the adsorption rate (2.5-2.6 mg / g) for copper and cadmium on pure cellulose and 4.2-4.6 mg / g for grafted cellulose. For chromium, the retention rate is extremely high at 10 mg / g for pure cellulose and 14 mg / g for the grafted cellulose. This is due to the reduction of chromium, which makes it more mobile and attracted by the material.

3.6.2 The influence of pH on the adsorption of Cd^{2+} , Cu^{2+} , Cr^{6+}

The pH has a certain influence on the process of the removal of metal cations in adsorption aqueous solutions, because it directly influences the surface charge and the nature of the ionic species of the adsorbents. In this

context, the effect of pH on the kinetics of retention was studied for the values of 2, 4, 6, 8, 10 and 12 for unbleached and grafted cellulose.

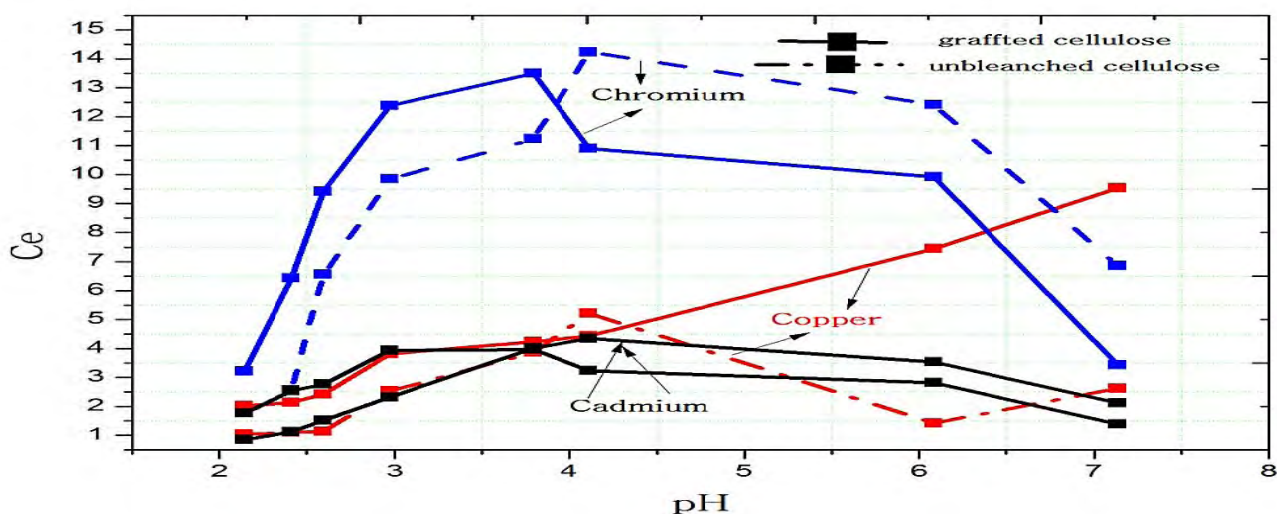


Fig. 5 The effect of pH on the retention of Copper ions: $C_0 = 20 \text{ mg / l}$, $T^\circ = 20 \pm 2^\circ \text{ C}$, $V \text{ agitation} = 350 \text{ rpm}$, $V = 25 \text{ ml}$, $\text{Time} = 60 \text{ min}$.

Fig. 5 shows that for unbleached cellulose the chromium (VI) removal capacity at equilibrium increases with pH from 2 to 7, and decreases when it is from 8 to 12. However, for the grafted cellulose the optimum pH is equal to 5 because of the presence of amide groups and the adsorption capacity is greater than that of the unbleached cellulose ($Q_e = 14.2 \text{ mg / g}$). At basic pH this might be due to the passage of the bichromate ion in an acid medium to the chromate ion in a basic medium; this type would not be adsorbed by the polymer.

It can be seen that the equilibrium copper (II) removal capacity increases with the initial pH from 2 to 7, but decreases from pH 8 to 12 for unbleached cellulose; therefore, the optimal pH is neutral. However, for the grafted cellulose the optimum pH is equal to 5 because of the presence of the amide group, while the adsorption capacity is maximal after one, with a decrease of the adsorption capacity with an increase in pH. The comparison equilibrium curves show that the capacity of the adsorption is minimal at $\text{pH} = 2$. On the other hand, by increasing the pH (4-5) and decreasing the pH (>8), the variation of the capacity between these pH values is slightly different. The maximum adsorption at $\text{pH} =$ for the material grafted with $Q_e = 14.5 \text{ mg / g}$ against $Q_e = 13.7 \text{ mg / g}$ at $\text{pH} = 4, 6$. In general, it is noted that the adsorption of the heavy metals under study is better for the grafted cellulose and with an acidic pH due to the presence of H^+ ions, which facilitate the formation of a covalent chemical bond between the H^+ ion and the metal; it is found that chromium has a certain affinity for cellulosic fibre since the adsorption is twice as great as that of the two other metals.

3.6.3 Effect of initial concentration on adsorption of Cd^{2+} , Cu^{2+} , Cr^{6+}

The initial concentration of the pollutant has a significant influence on the retention capacity of the solid support. In order to study its effect, the following values were considered: 5, 10, 20, 30, 40, 50, 60 and 100 mg / l.

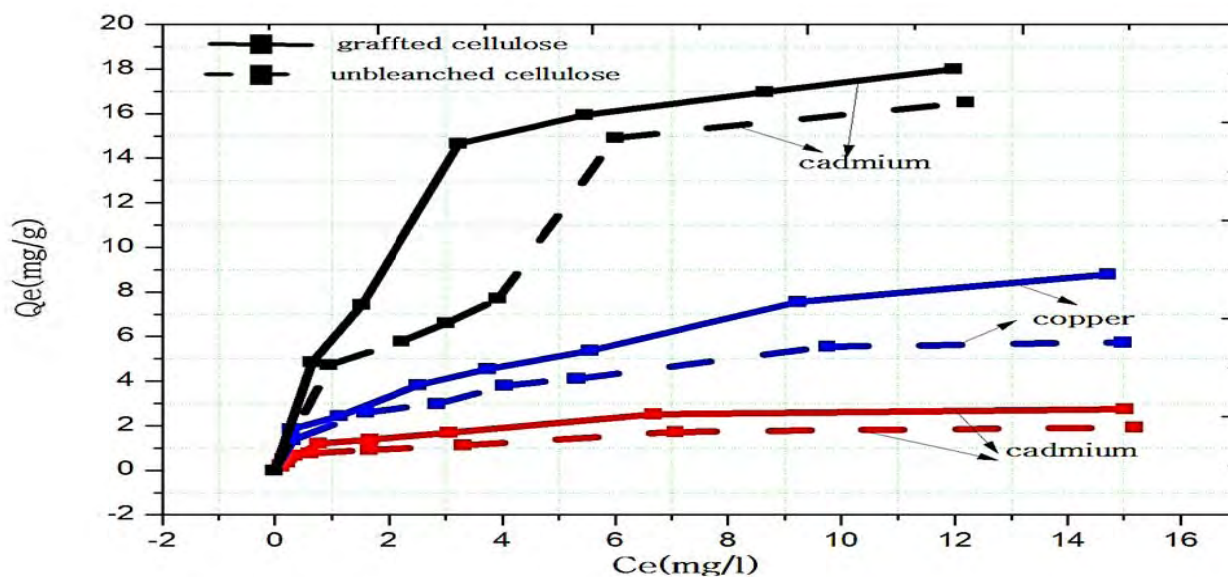


Fig. 6 The effect of the concentration on the retention of Copper ions: $T = 20 \pm 2^\circ \text{C}$, V agitation = 350 rpm, $V = 25$ ml, Time = 60 min, $\text{pH} = 5.33$

The results obtained are shown in Fig. 6. For copper, the data show that the adsorption capacity increased with the initial concentration of the metals studied and reached 6.5 mg / g for the grafted cellulose and 4 mg / g for the pure cellulose, evidencing greater availability of the sites' adsorption valences and some ions tend to form other particles in the solution

For chromium, the evolution of adsorption was quite different; it rapidly attained a concentration of around 20 mg / l) and then the adsorption appeared to be multi-layered and stabilized at 13.7 mg / g, for pure cellulose, which seemed saturated but evolved gradually to the grafted cellulose until a 19.7 adsorption mg / g. The presence of active sites was the main factor in the increased adsorption, with input connections free from H^+ and carboxyl groups of organic matter, oxides (Godfri and Bladel, 1990; Gould and Genteelly, 1998).

Regarding the retention of cadmium, it followed a sigmoidal pattern, showing a two-stage multilayer adsorption with a higher yield for the grafted cellulose. This was probably due to the modes of attachment of metal ions and the affinity of the adsorbent, which is oriented towards the cadmium ion and releases carboxylic ions and OH.

It should be noted that for high concentrations, the driving force due to the concentration gradient is higher, and the number of ions adsorbed per unit mass of adsorbent, Q_e , is greater, which causes a saturation of support. Thus a quantity of the ions remains free in the solution, giving a weak yield (Babu et al., 2013).

We concluded that the adsorbent cellulose (unbleached and grafted) was more effective for wastewater with low concentrations of metal ions, and the purification efficiency could be increased by diluting the wastewater containing high concentrations.

3.6.4 The influence of ionic strength on the adsorption of pure and grafted cellulose

To study the influence of ionic strength on the efficiency of cadmium copper and chromium, they were used with defined weights of potassium chloride "KCl" (solid) at a concentration of metal ion at 1000 mg / l. (15, 30, 60, 120, and 180 ml) with solutions of three different ionic strengths (1, 2 and 3 M / l).

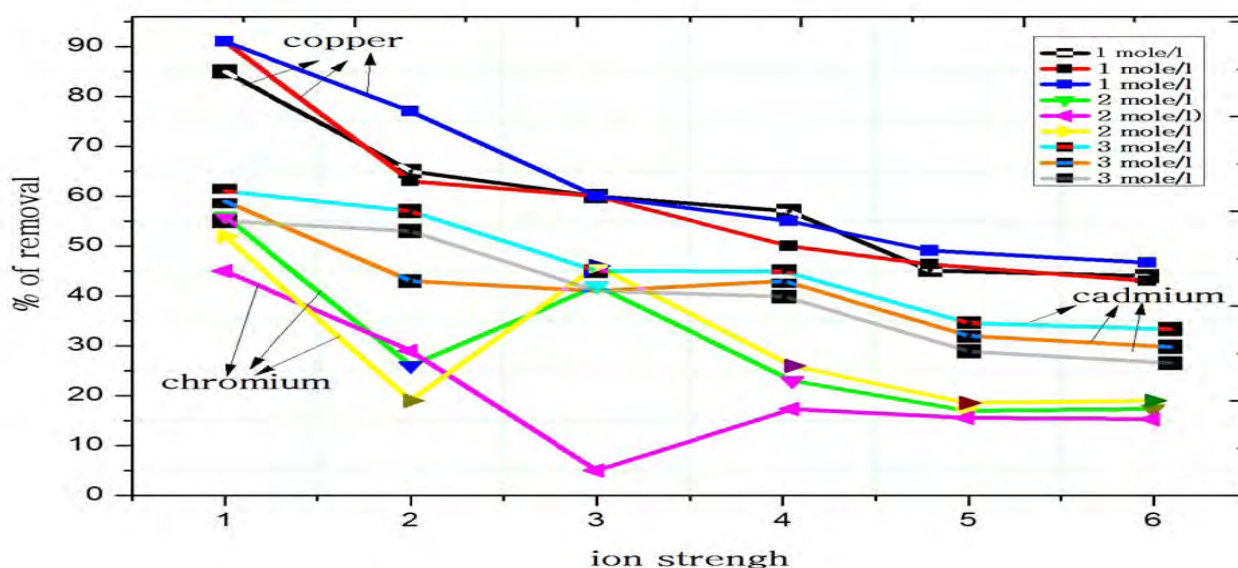


Fig. 7 Effect of ion strength on the efficiency Metals at the concentration of solution (1M/l)(2M/l) and (3 M/l).

The results of each experiment were calculated and presented in Fig.7. As shown the increase in ionic strength led to a decrease in the number of adsorbed metal ions resulting from the competition between these metal ions and salt ions (Ho et al., 2001; Kolasniski, 2001; Oliveira et al., 2008). The reduction in absorption was probably due to the activity of the K^+ ions, which inhibit the approach of the Cr, Cd and Cu ions to the active sites of the adsorbent. An increase can influence the adsorption of metal ions on cellulose and grafted cellulose in three possible ways:

-Decrease the activity in the solution of metal ions.

-Increase the concentration of competing ions (K^+). With the increase of I, there is a slight decrease in the removal of metal ions, which can be attributed to the presence of adsorption sites of different affinities.

-The distributions and rates of the specific surfaces of (micropores, pores and mesopores) the ions studied.

3.7 The adsorption isotherms of the three metallic elements (Cd, Cr, Cu)

3.7.1 Cadmium isotherms adsorption

About the adsorption isotherms of cadmium on the pure and grafted cellulose, Fig.8(a) indicates that the cellulose support has a good affinity for Cd^{2+} , where two distinct zones are noted: the first, the adsorption capacity of which increases with the initial concentration, and the second or saturation plateau. These isotherms showed a rapid increase in the amount of Cd^{2+} adsorbed in solutions with low concentrations, followed by a slight increase until a plateau corresponding to a saturation of the adsorption sites was reached. This is explained by the formation of a monolayer. This led to the conclusion that the isotherms obtained are similar to the L type according to Gill.

For all samples, the data show that the adsorption capacity of the metal increases with the increase of the initial Cd^{2+} concentration. The retention yield Fig. 8(b) and (c) shows that after an increase of between 5 and 20 mg / l concentrations, it decreases from the concentration of 35 mg / l. This is explained by the fact that at low concentrations the ratio between the active sites of the adsorbent and the metal ions in the concentrated solution is so all the metal ions can be retained by the adsorbent and completely removed.

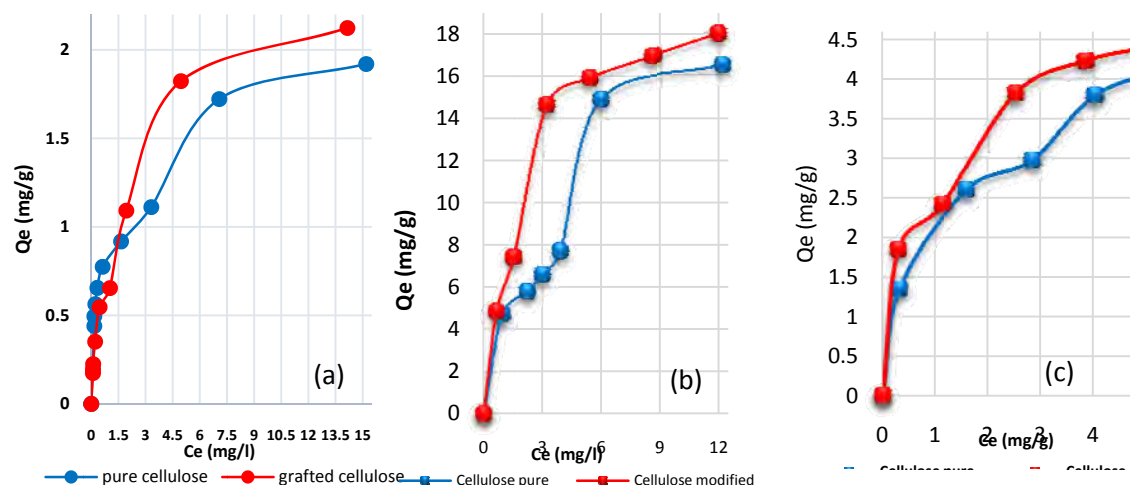


Fig. 8 Isotherm of adsorption of: Cadmium (a) chromium (b) Copper: (c). $T^\circ = 20 \pm 2^\circ\text{C}$, $V_{\text{agitation}} = 350$ tr/min, $V = 25$ ml, Time = 60 min, pH = 5.33 (grafted cellulose) et pH = 7 (pure cellulose).

3.7.2 Chromium adsorption isotherms

Fig. 10 shows the adsorption isotherms of copper on the unbleached and grafted cellulose. The cellulosic support had a good affinity with the Cu^{2+} cation and there appeared to be two distinct zones: the first, the adsorption capacity of which increased with the initial concentration, and the second or saturation plateau. These isotherms showed a rapid increase in the amount of Cu adsorbed in the solution with low concentrations, followed by a slight increase until a plateau was reached corresponding to a saturation of the adsorption sites, which appeared to be a multilayer adsorption. The isotherms obtained were similar to type S, according to the Gills isotherm classification.

3.7.3 Copper adsorption isotherms

Fig 9 shows the isotherm adsorption of copper on the unbleached and grafted cellulose. The cellulosic substrate had a good affinity for the cation Cu^{2+} , or we can see two separate areas: the first, in which the adsorption ability increased with the initial and second concentrations, and the second, in which saturation plateaus were reached. These isotherms showed more or less rapid increases, depending on the amount of adsorbed Cu, with low concentrations followed by a slight increase until a plateau corresponding to a saturation of the adsorption sites was obtained. The adsorption, in monolayer, was similar to type L according to Gills' classification.

3.8 Kinetic constants and correlation factors of different adsorption isotherms of Cd^{2+} , Cr^{6+} and Cu^{2+} on cellulose (pure and grafted)

In order to identify the retention mechanism of the initial concentration ($C_0 = 5$ to 100 mg / L), and to identify the isotherm representing better the adsorption of copper ions on the grafted cellulose, six theoretical models (Freundlich, Langmuir, Temkin, Elovich, Dubinin-Radushkevich (D-R) and Redlich-Peterson (Freundlich, 1906; Temkin, 1941; Elovich and Larinov, 1962; Redlich and Patterson, 1959) were tested and the experimental results are given in Table 5. It follows from the theory of Langmuir and Redlich-Peterson that in our case a formation of more than a monolayer adsorption on the surface may be possible and sites are heterogeneous with differing mounting energy.

3.9 Validation of kinetic models

Kinetic data obtained for the adsorption process were analysed on the basis of the three most used models. In order to identify the retention mechanism for initial concentrations ($C_0 = 5$ to 100 mg / L), and to identify the

isotherm that best represents the adsorption of chromium VI ions on unbleached and grafted cellulose, six models' theoretical tests were performed on the experimental results obtained (Freundlich, Langmuir, Temkin, Elovich, D-R and Redlich-Peterson).

Considering the graphical representation of each isotherm (Fig. 9(a)-(c) and Table 5), which provides the correlation factors, as well as the constants of each model, it is obvious that the mechanism of retention of chromium ions is represented by the Redlich-Peterson isotherm for unbleached cellulose and by the Langmuir isotherm for grafted cellulose, which is the highest correlation factor compared to the other models.

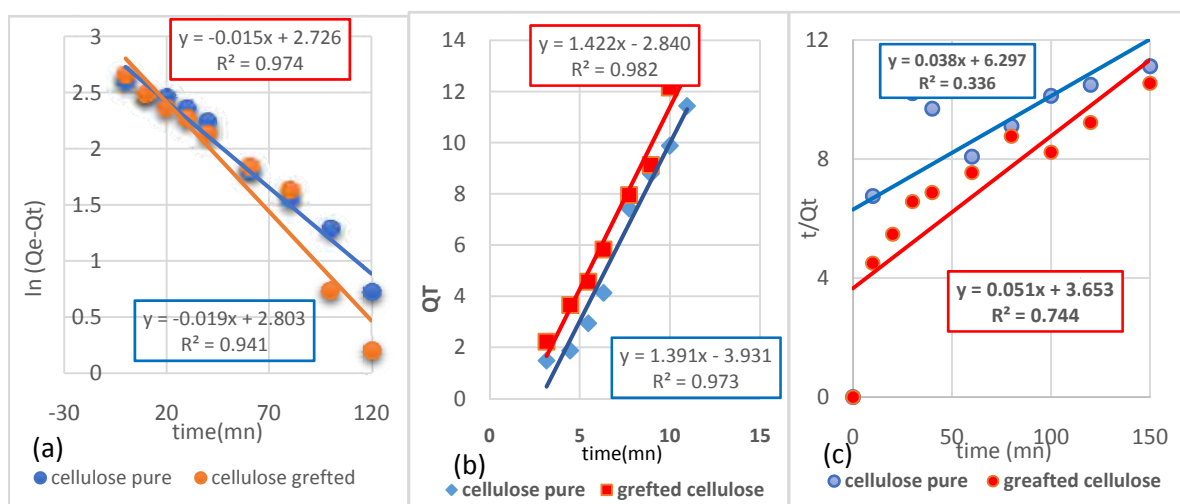


Fig. 9 Linearization of the chromium retention kinetics of pseudo first order, for cellulose retention of Cr(a) , pseudo second order(b), intra-particle diffusion('c) models for cellulose retention of Cr (pure and grafted cellulose: (pure and grafted cellulose): $C_0= 20$ mg/l, $V_{agitation}=350$ tr/min, $T= 20\pm 2^\circ C$, $=25$ ml.

(1) Pseudo-first-order model

The validity of the Lagergren equation was first tested by plotting 'ln (qe -qt)' versus t. Fig. 9(a) shows that the experimental results obtained follow perfectly the linear variation given by the equation representative of pseudo-first-order kinetics. The value for the constant k1 for cellulose is shown in Table 5.

(2) Model of pseudo-second-order kinetics

From the equation representative of the pseudo-second-order kinetics and its linear form, the speed constant K_2 can be computed graphically by plotting qt / t as a function of t. Fig. 9(b) shows that the Lagergren equation is not applicable in the case of cadmium retention for both unbleached and grafted cellulose.

(3) Model of intra-particle scattering

The application of the equation for intra-particle diffusion to the experimental data by plotting qt according to $t^{0.5}$ suggests the applicability of the intra-particle diffusion model governing adsorption kinetics. Thus, the curves presented below show the kinetics of intra-particle diffusion for unbleached and grafted cellulose. As the curves in Fig. 9(c) indicate, there is continuous linearity along the process.

For the diffuse layer model, the slope of the linear part of the curve has been calculated and represents the kinetic constant k_{int} .

Table 6 Parameters of kinetic models studied for chromium.

	Constants	Pure cellulose	Grafted cellulose
Kinetics of the first order	K1 (min ⁻¹)	0.0153	0.0194
	Qe (mg/g)	15.43904	16.5023
	R ²	0.94774	0.941
Kinetics of the 2nd order	K2 (min ⁻¹)	0.00606	0.01402
	Qe (mg/g)	5.11644	4.41941
	R ²	0.3362	0.7449
Diffusion intra particule	kint (mg/g.min ^{0.5})	1.3911	1.4229
	R ²	0.9737	0.9827

3.10 Adsorption kinetics of copper

From the graphical representation of each isotherm (Fig.10(a)-(c) and Table 7), which gives the correlation factors as well as the constants of each model, it is obvious that the retention of cadmium ions is represented by the Redlich-Peterson isotherm for unbleached cellulose and the Langmuir isotherm for grafted cellulose, which is the highest correlation factor compared to other models.

Kinetic data obtained for the adsorption process were analyzed using the three most common models. The kinetics of copper was studied for unbleached and grafted cellulose at a concentration of 20 mg / l of solution.

The validity of the Lagergren equation was first tested by plotting $\ln(q_e - qt)$ versus t . From Fig. 10, it is clear that the Lagergren equation is not applicable in the case of copper retention for unbleached cellulose.

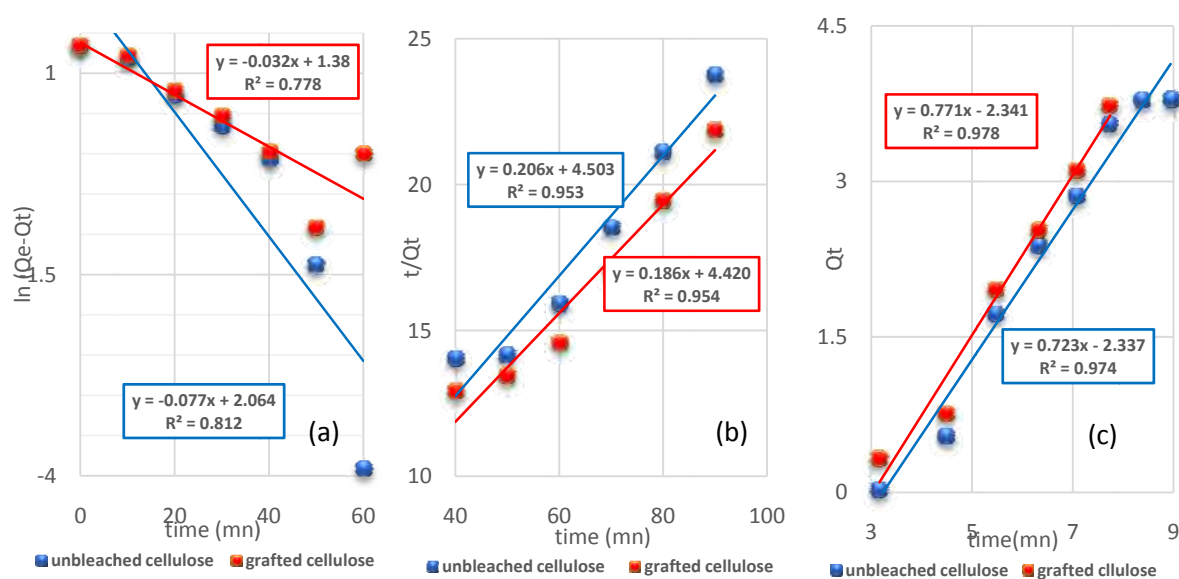


Fig. 10 Linearization of the pseudo-first order retention kinetics: copper (a) pseudo second order (b) intra-particle diffusion (c) $C_0 = 20$ mg / l, pH = 7 (pure), pH = 5 (grafted), V agitation = 350 rpm, $T = 20 \pm 2$ ° C, $V = 25$ ml.

From the equation representative of pseudo-second-order kinetics and its linear form, the speed constant k_2 can be calculated graphically by plotting qt / t as a function of Fig. 10(b) and shows that the experimental results obtained follow the linear variation perfectly, given by the equation representative of pseudo-second-order kinetics, and the value for the constant k_2 for cellulose as shown in Table 7.

The application of the intra-particle diffusion equation to the experimental data, plotting qt as a function of time, suggests the applicability of the intra-field diffusion model governing adsorption kinetics. Thus, the curves presented below show the kinetics of the intra particle diffusion to the unbleached and grafted cellulose. As indicated by the curves in Fig. 10(c), there is no continuous linearity along the process. So, just apply the linear regression to the most linear slice.

Table 7 Parameters of kinetic models studied for copper.

	Constants	Pure cellulose	Grafted cellulose
Kinetics of the first order	K_1 (min^{-1})	0,0773	0,0323
	Q_e (mg/g)	7,8829	3,9749
	R^2	0,8124	0,7788
Kinetics of the 2nd order	K_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$)	0,31749	0,31244
	q_e (mg/g)	2,2027	2,317445
	R^2	0,9531	0,9547
Intra particle diffusion	k_{int} ($\text{mg/g} \cdot \text{min}^{0.5}$)	0,7232	0,7717
	R^2	0,9745	0,9781

3.11 Adsorption kinetics of cadmium

In order to identify the retention mechanism for initial concentrations ($C_0 = 5$ to 100 mg / L), and identify the isotherm that better represents the adsorption of cadmium ions on unbleached and grafted cellulose, six theoretical models were tested on the experimental results obtained, namely Freundlich, Langmuir, Temkin, Elovich, D-R and Redlich-Peterson.

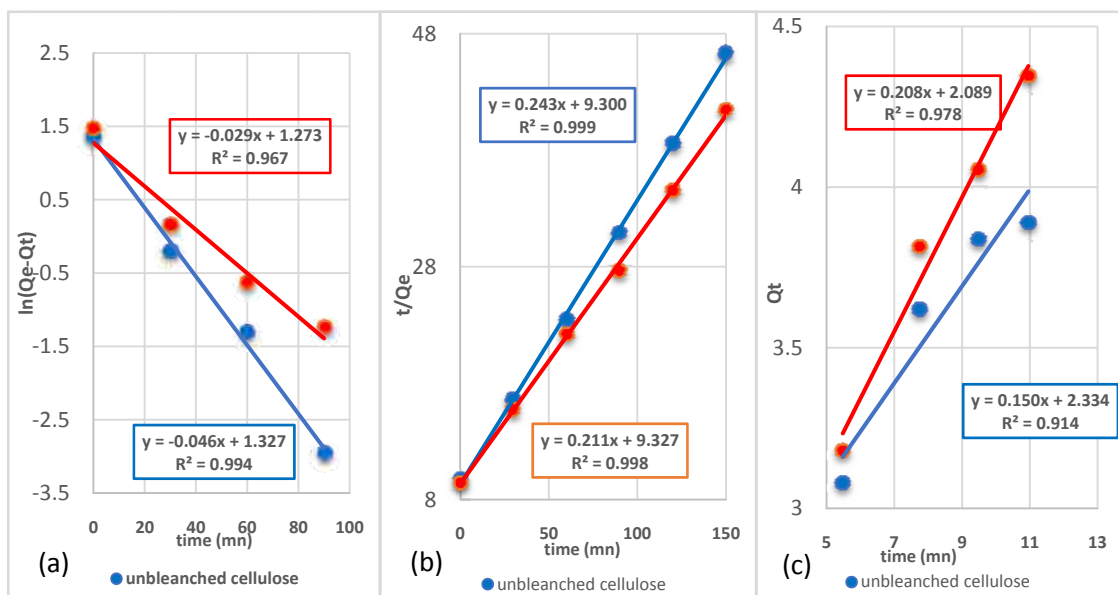


Fig. 11 Linearization of: cadmium , pseudo-first order retention kinetics (a) pseudo second order (b) intra-particle diffusion(c) $C_0 = 20\text{mg} / \text{l}$, V agitation = 350 rev / min, $T = 20 \pm 2^\circ \text{C}$, $V = 25\text{ml}$ $20\text{mg} / \text{l}$, $\text{pH} = 7$ (pure) and $\text{pH} = 5.33$ (grafted).

From the graphical representation of each isotherm (Fig.11(a)-(c) and the Table 8), which shows the correlation factors, as well as the constants of each model, it is obvious that this mechanism of The retention of cadmium ions is represented by the Redlich-Peterson isotherm for unbleached cellulose and the Langmuir isotherm for grafted cellulose, which is the highest correlation factor, compared to other models. Therefore, according to the Redlich-Peterson and Langmuir theory, the case of a formation of more than one adsorption monolayer on the surface may be possible and the sites are heterogeneous, with differing binding energies.

Table 8 The kinetic constants and correlation factors of differing Cd adsorption isotherms on cellulose (pure and grafted).

Isothermal Type	Constants	Pure Cellulose	Grafted Cellulose
Langmuir	q_m (mg/g)	2,003205	2,32342
	K_L (L/mg)	0,920014	0,695427
	R^2	0,9789	0,9927
Freundlich	K_f (mg ¹⁻ⁿ · l ⁿ · g ⁻¹)	0,84806	0,70419
	n_f	0,3071	0,4968
	R^2	0,9782	0,9729
Temkin	B_T (mg/g)	2,9043	3,62368
	K_T (L/mg)	0,3764	0,46351
	R^2	0,939	0,9609
Elovich	K_E (L/mg)	-0,476871	-0,83160
	q_m (mg/g)	-0,32723	-0,51345
	R^2	0,9155	0,9639
Dubinin-Radushkevich	q_{mDR} (mg/g)	1,30343	1,30931
	β	1,8623	1,3256
	R^2	0,8024	0,9002
Redlich-Peterson	n	0,6929	0,4832
	$\ln(K_L^{n-1}/q_m)$	-0,5347	-0,01257
	R^2	0,9956	0,9691

The kinetic data obtained for the adsorption process were analyzed using the three most common models. The kinetics of cadmium was studied for unbleached cellulose at a concentration of 20 mg / l.

The validity of the Lagergren equation was first tested by plotting $\ln(q_e - qt)$ versus t . Figure 11(a), shows that the experimental results obtained follow perfectly the linear variation given by the equation representative of a kinetic pseudo-first-order. The value for the constant k_1 for the cellulose is shown in Table 8.

From the equation representative of the pseudo-second order kinetics and linear form, the constant k_2 speed can be calculated by graphically plotting qt / t vs. t . Fig. 11(b) shows that the Lagergren equation is applicable in the case of cadmium retention for both unbleached and grafted cellulose.

The application of the intra-particle diffusion equation to the experimental data, plotting qt versus $t^{0.5}$, suggests the applicability of the intraparticle scattering model governing the adsorption kinetics. Thus, the curves presented below show the kinetics of intra-particle diffusion for unbleached and grafted cellulose. From the curves off Fig. 11(c), it is noted that there is continued linearity throughout the process.

For the diffuse layer model, the slope of the linear part of the curve was calculated and represents the kinetic constant k_{int} .

Table 9 Parameters of the kinetic models studied for cadmium.

	Constants	Pure cellulose	Grafted cellulose
Kinetics of the first order	K_1 (min^{-1})	0,0468	0,0296
	Q_e (mg/g)	3,57405	3,7727
	R^2	0,9947	0,9673
Kinetics of the 2nd order	K_2 ($\text{g.mg}^{-1}.\text{min}^{-1}$)	0,01156	0,01149
	q_e (mg/g)	3,7555	3,145027
	R^2	0,9992	0,9989
Intra particle diffusion	k_{int} ($\text{mg/g.min}^{0.5}$)	0,1508	0,2087
	R^2	0,9148	09788

4 Conclusion

The aim of this work was to confer new properties on a cellulosic fibrous material by means of the chemical grafting of acrylic functions for the treatment of effluents containing inorganic pollutants (heavy metals) as part of a process research approach to potentially applicable to wastewater treatment. This work was also an opportunity to understand the method of fixing the inorganic contaminants of these materials in aqueous solutions.

To confirm the new properties of the grafted material, having a high absorbency, a physicochemical characterization was achieved and the following observations can be made:

The spectrum of the Fourier transformed by infrared rays confirms the appearance of new bands characteristic of copolymerization.

When observed under a scanning electron microscope, the grafted fibres showed a modification of their morphology. Grafting on cellulose inherently reduces the fibre structure, which favors the growth of less structured amorphous areas for enhanced absorption.

The results showed that the retention of metal ions was extremely rapid, reaching equilibrium after 60 minutes for copper, and 120 to 150 minutes for cadmium and chrome on cellulose (unbleached and grafted).

The pH effect study demonstrated that the removal rate of heavy metals (Cr^{6+} , Cu^{2+} , and Cd^{2+}) peaked at pH 8-10 for unbleached cellulose. However, it gave a better performance and better retention in acidic areas (5-7) of grafted cellulose. The effect of the initial concentration, as well as the solid / liquid ratio for the dye, was also examined.

The results of the kinetic study for all the heavy metals demonstrated that the retention was extremely fast. In fact, it was almost instantaneous. Linear regressions have shown that kinetics is controlled by the pseudo-second-order model, so the chrome is controlled by the pseudo-first-order model. This was clearly confirmed by the values of the correlation factors corresponding to each model.

The adsorption isotherms for cadmium and chromium concentrations chosen for initial experimental data were interpreted by the Redlich-Peterson and Langmuir models for unbleached cellulose for the grafted cellulose. For copper, the Freundlich model best described the data for adsorption isotherms on unbleached cellulose and the Redlich-Peterson and Langmuir models for retention of copper for the grafted cellulose.

This work is interesting because it targets two objectives, the first is environmental, because it emerges very toxic heavy metals, using the cellulose from the waste of the cotton factories, and the second is economic, because the cost of the operation is low.

Acknowledgement

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