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MODIFIED CELLULOSE WITH TERTIARY AMINE AND SCHIFF BASE CHELATING SITES FOR THE REMOVAL OF HEAVY METAL IONS FROM AQUEOUS SOLUTION

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ABSTRACT

Cellulose being the most abundant, renewable and natural green raw material has the potential application in adsorption of heavy metal ions. Among the various chelating groups in a cellulose matrix, the capacity of the $–N(CH)_3$ and –N=CH- chelating groups are higher and hence their binding capacity towards the metal ions are better. Cellulose bearing $–N(CH_3)_2$ and –N=CH– chelating groups (Cell-TA) was synthesized through two step chemical reaction process and its adsorbing efficiency towards the Pb(II), Cu(II) and Ni(II) metal ions from aqueous solution was evaluated. The structural characteristics and the metal ion adsorbing features are examined through FT-IR, isotherm and kinetic models with thermodynamic studies.

Keywords: Cellulose, Schiff base, Spectral studies, Thermodynamics.

INTRODUCTION

In recent years, the removal of hazardous heavy metals from industrial, domestic, agricultural, medical and technological applications has attracted worldwide concern. The rising levels of mobile and soluble heavy metal species is a serious problem, owing to their high degree of toxicity (Herica et al., 2012). The metals of major concern are Al, Cd, Co, Cu, Pb, Mn, Hg, Ni and Zn. Mining, electroplating, metal processing and battery manufacturing are the major sources of heavy metal contamination (Ellchi and Tetsuo, 1984). Various treatment methods have been employed to remove metal pollutants from an aqueous media such as chemical precipitation, coagulation, ion exchange etc (Shiyan et al., 2009). Among these various treatment methods the well-recognized and most effective method for the removal of heavy metals is adsorption. The adsorption of heavy metal ions by the polymeric adsorbents based on the polymers and the chemical modification of cellulose is successfully reported. (Murugesan et al., 2011; Dinesh Kirupha et al., 2013; Ravikumar et al., 2010; Kalaivani et al., 2014a) and chemically modified cellulose (Saravanan and Ravikumar, 2015). The natural products or the waste materials from the industries received a great attention towards the ecofriendly approach, to remove Pb(II), Cu(II) and Ni(II) from the waste water. Cellulose based derivatives because of their presence of hydroxyl groups received a great attention. The Dialdehyde cellulose was prepared by the periodate oxidation of cellulose which was further oxidized by using mild acidic sodium chlorite. (Rutherford et al, 1942). The cellulose in the form of the filter sheets was effectively used as the adsorbent for the removal of heavy metal ions from the waste water. (Batmaz, 2014, Foglarova 2009, Mackewa et al., 1990). Furthermore, oxycellulose was applied in an ion exchange column and in a batch process for the removal of heavy metal ions. (Foglarova 2009). Therefore, the need for low cost solid adsorbents based on natural or synthetic polymers is ever growing. The selective removal of Pb^{2+}, Cu^{2+} and Ni^{2+} heavy metals by chemically modified cellulose hybrid materials (Sun and Wang, 2006) have received great consideration. The aim of the present work is to synthesize chemically modified cellulose (Cell-TA) and examine its metal ion uptake by using Pb^{2+}, Cu^{2+} and Ni^{2+} ions. The various parameters such as solution pH, contact time, adsorbent dosage, initial metal ion concentration, temperature, regeneration of the sorbent material have been investigated.

EXPERIMENTAL

Chemicals and reagents

Cellulose (Loba), sodium meta periodate (Sigma Aldrich), *N*,*N*-dimethyl aniline (Fluka) , and the $CuSO_4 \cdot 5H_2O$, $Pb(NO_3)_2$,$NiSO_4 \cdot 7H_2O$ salts were acquired from Aldrich-Sigma Chemical, India. All the chemicals and reagent used for the experiment and the analysis were of an analytical grade. The stock solutions of 1000 mg/L of standardized $Pb^{2+,}$ Cu^{2+}, and Ni^{2+} ions were prepared by dissolving the appropriate amount of the respective salts in distilled water

Synthesis of chemically modified cellulose: (Cell-TA)

Typically 5 gm of cellulose powder suspended in double distilled water is mixed with 0.03 N sodium Meta periodate solution and stirred at room temperature in dark for 4 h. On an average 30 carbonyl groups / 100 glucose units are achieved under these reaction conditions. After 4 h, the formed dialdehyde cellulose was filtered and washed with double distilled water until the achievement of neutral conditions. The dialdehyde cellulose was dried under vacuum for 3 h. The obtained dark brown colored product was filtered and washed several times with double distilled water followed by ethanol and dried under vacuum.

Batch adsorption studies

The batch adsorption experiments were conducted using 20 mL of the metal solutions of lead, copper and nickel containing 40 mg of the Cell-TA is flustered, in a conical flask using a horizontal bench shaker (Orbitek - Teqip-ACT/EQ/454) at a speed of 200 rpm. The influence of the hydrogen ion concentration on the adsorption of

Cell-TA on to the metal ion uptake was carried out by varying the pH from 2 to 10 using 0.1 M HCl and 0.1 M NaOH with the initial metal solution of 20 mg/L concentration at ambient temperature. The solution pH of the metal ions was monitored before analyzing every parameter and reformed to its initial value. For the isotherm studies, the metal ion concentration bounding between 20- 100 mg/L were used. The contact time of 1 h was preferred to attain adsorption equilibrium state with 10 min as interval time. .

RESULTS AND DISCUSSION

Characterization of the Cell-TA

The IR spectra of the synthesized Cell-TA with the metal ions are given in figure 1.

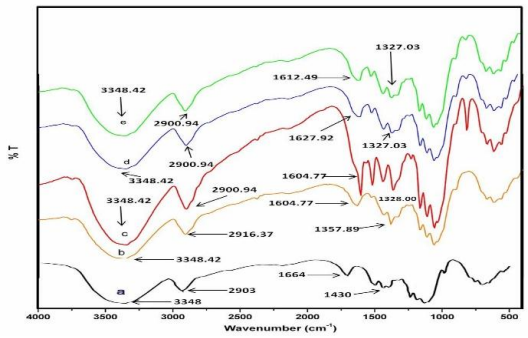

Fig 1: FT-IR Spectrum of (a)Cellulose (Cell) , (b) Cell-TA (c) Cell-TA-Cu (d) Cell TA-Ni (e) Cell TA-Pb.

In the chemically modified cellulose, due to the cleavage of C_2-C_3 bonds and subsequent formation of (-CH=N-) schiff base the C-C ring frequency was shifted from 1430 cm^{-1} to 1357 cm^{-1} as the imine -CH frequency appeared at 2916 cm^{-1}. The azomethine (-CH=N-) stretching frequency was clearly observed as a new peak at 1604 cm^{-1}. These observations support the structure of chemically modified cellulose (Cell-TA).

EFFECT OF SOLUTION pH

The influence of hydrogen ion concentration on the adsorption of Pb^{2+}, Cu^{2+} and Ni^{2+} ions was investigated by varying the pH of metal solution in the range of 2.0 –10 . The results obtained in Figure 2 shows that the adsorption capacity increases rapidly from a pH value of 2 to 5 and remains almost constant after the pH value of 6. The maximum removal efficiencies of Pb^{2+}, Cu^{2+} and Ni^{2+}ions were 98.87 %, 85.84% and 94.92 % respectively.

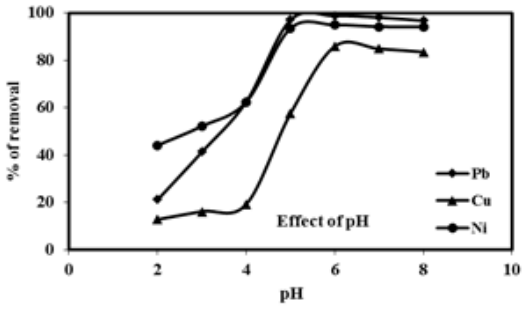

Fig 2: Effect of pH onto Pb (II), Cu (II) and Ni (II) metal sorption by Cell-TA (Initial metal ion concentration=100 mg/L, adsorbent dose=40 mg/L and Contact time=60 min)

EFFECT OF CONTACT TIME AND ADSORPTION KINETICS

The adsorption experiments were carried out under optimized conditions and investigated up to 1h with 10 min interval time and the results presented in Figure 3.

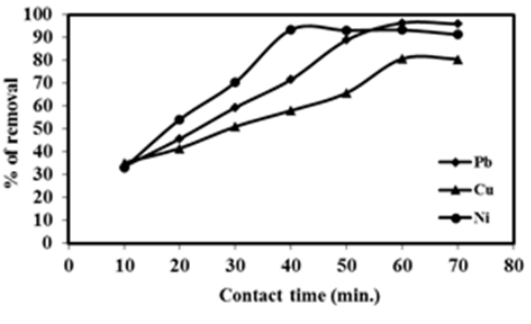

Fig 3 : Effect of contact time onto Pb(II), Cu(II) and Ni(II) metal ion by Cell- TA (Optimized adsorbent dose = 40 mg/L, optimized pH=6 and Optimized initial metal ion concentration = 100 mg/L)

The metal ion removal was fast for 20 min due to the possibility of more number of adsorption sites on the surface of the Cell-TA and slowly reaches the saturation point at 1 h. The (R^2) value was found to be low and the q_e exponential value contradict from the q_e calculated values .Investigating the uptake - time curves shows that the co-relation coefficient found to be high follows the order of Pb^{2+}>Cu^{2+}>Ni^{2+} ions by Cell-TA when calculated and experimental q_e values were computed. These measurements suggest that adsorption of metal ions on to Cell-TA follows, the pseudo second order kinetic model with the chemisorption as the rate determining step. From the kinetic data obtained for the polymeric adsorbent Cell-TA, the metal ions stick to the surface which forms a chemical bonding tends to find the their sites. (Atkins, 1995)

Table 1: Kinetic parameters for the adsorption of Pb(II), Cu(II) and Ni(II) metal ions on to Cell-TA

Kinetic model	Parameter	Pb(II) Ni(II)		Cu(II)
Pseudo-First order	$K_{(ad)}$ (min^{-1})	2.57 x 10^{-2}	2.3 x 10^{-2}	1.8 x 10^{-2}
	q_e cal(mg/g)	2.00	1.94	1.80
	R^2	0.9566	0.9497	0.9190
Pseudo-Second order	K(g $mg^{-1}min^{-1}$)	0.0096	0.0094	0.011
	q_e Cal(mg/g)	10.67	10.28	7.48
	R^2	0.9969	0.9968	0.9910

EFFECT OF INITIAL ION CONCENTRATION AND ADSORPTION ISOTHERM

The adsorption capacity of the adsorbent (Cell-TA) , was evaluated to design, understand the adsorption isotherm process. The percentage removal of metal ions such as Pb^{2+}, Cu^{2+} and Ni^{2+} at different metal ion concentration (20– 100 mg/L) using Cell-TA is presented in Fig.4**.** The initial metal ion concentrations were increased from 20 to 100 mg/L, the percentage of adsorption was slightly decreased due to the saturation of active adsorption sites on to Cell-TA.The Freundlich adsorption isotherm fits to be the best model and favourable where the value of n (1<n<10), indicating the adsorption of metal ion to adsorbent .The decrease in the adsorbent-adsorbate interaction with increasing surface density is common and due to a distribution of surface sites (Diner et al., 2007) (Nicki 2008, Subramanian, 2009)

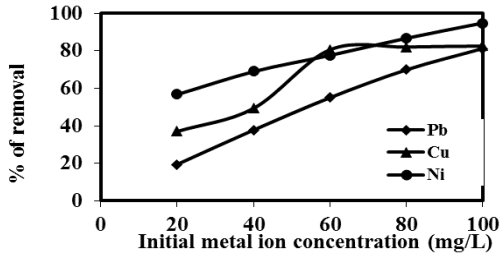

Fig 4 : Effect of initial metal ion concentration onto metal sorption Pb(II),Cu(II) and Ni(II) on to Cell-TA (Optimized adsorbent dose = 40 mg/L, optimized pH=6 and Contact time=60 min)

EFFECT OF TEMPERATURE

The effect of the temperature on the adsorption of Pb^{2+}, Cu^{2+} and Ni^{2+} ion on to the Cell-TA has been calculated at 303,308,313, 323 K . The decrease in the adsorption capacity of PoU resin with constant range increase in temperature from 30˚ C to 60˚C (McKay 1980, ozer, 2006). The thermodynamic criterions such as Gibbs free energy change ΔG0, the enthalpy change ΔH, and the entropy change ΔS^0 were calculated The negative values of ΔH showed the adsorption of Where K_C is the equilibrium constant, Ce is the equilibrium metal ion concentration in solution ions on to the Cell –TA is exothermic in nature. The negative ΔG values at all the studied temperature suggest that the adsorption process was feasible and spontaneous.

CONCLUSION

Azomethine (-N=CH) and tertiary amine (-$N(CH_3)_2$) chelating groups were successfully introduced into a cellulose matrix and the solid adsorbent was used for the $Pb^{2+,}$ Cu^{2+} and Ni^{2+} ions metal ion uptake studies in aqueous media. From the isotherm models, kinetic models and thermodynamic studies it is suggested that the adsorption process is multilayer and reversible chemisorption. From FT-IR analysis, it is suggested that the –N=CH- and –$N(CH_3)_2$ are the main chelating sites. The green cellulose adsorbent is an efficient one and is safe in handling and after use disposal can be a potential candidate for the removal of toxic heavy metal ions removal from aquatic environment.

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