



Starch Based Chitin Ternary Blend for the Removal of Contaminants from Textile Wastewater

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ABSTRACT

Industries are essential for economic development of any country. Textile industry is one of the most important and rapidly developing industrial sectors. Effluent generated for the textile industry is one of the sources of pollution. The textile effluents were collected from Ranipet area and the collected wastewater is analyzed for the major water quality parameters, such as Biological Oxygen Demand (BOD), pH, Chemical Oxygen Demand (COD), Total suspended solid (TSS) and Total Dissolved Solids (TDS) and metal ions such as Cr, Pb, Zn, Ni etc. starch based chitin ternary blend was prepared for the removal of contaminants from the effluent. Batch adsorption studies were performed under different environmental conditions of pH, adsorbent dose and contact time. The data was fitted with the kinetic models of pseudo first order and pseudo second order.

Keywords: Chitin; Starch; Cellulose fiber; Blend; Adsorption kinetics

INTRODUCTION

Textile wastewater includes a large variety of dyes and chemical additions that make a serious environmental issue for the last few decades [1]. Main pollution in textile wastewater comes from dyeing and finishing processes. In the dyeing process the average rate of used dye is around 85-90% and the unused residual dye of about 10-15% was contaminated in the water [2].

As a result the textile dyeing wastewater contains a large amount of complex components with high concentrations of organic, high-color and changing greatly the physico-chemical parameters such as suspended solids, dissolved oxygen, sulphate, sulphide, chloride, biological oxygen demand, chemical oxygen demand, copper lead, nickel and chromium from their normal prescribed levels [3]. Mond et al (2005) [4] reported that this diversity in physical, chemical, and biological characteristics of dyeing effluent is so much and it is necessary to develop the most suitable treatment techniques to treat the textile effluent. In recent years, adsorption has become one of the efficient treatment methods for wastewater laden with heavy metals. The search of adsorbents which are economically feasible with low cost and good chelating capacity to bind the metal ions has intensified [5]. The adsorbents may be of organic or biological origin, industrial byproducts, agricultural wastes, biomass, and polymeric materials [6].

Technical applicability and cost-effectiveness are the key factors that play major roles in the selection of the most suitable adsorbent to treat inorganic effluent. Chitin (β -(1-4)-poly-N-acetyl-D-glucosamine) is widely distributed in nature and is the second most abundant biopolymers in the biosphere [7]. Chitin has been recommended as an excellent adsorbent in many research papers, because of its unique properties such as biodegradability, chelating capacity, flocculating ability and its possibilities of regeneration in a number of applications [8]. Many research works has been developed using chitin for the wastewater treatment. The other polymers used in this study are starch and cellulose fiber/sisal fiber. Starch is a renewable and biodegradable polysaccharide generally employed as sorbent in the presence of crosslinker. Generally the crosslinked starches possess superior properties in aspects of

mechanical, thermal and chemical resistance [9, 10]. Cellulose was processed from sisal fiber. These fibers have abundant and specific functional group such as hydroxyl groups which have affinities for heavy metal ions [11]. In our study, a novel polymer blend chitin/starch/cellulose fiber crosslinked with glutaraldehyde has been used for the treatment of textile wastewater.

MATERIALS AND METHODS

Materials

Corn starch (12% moisture) was obtained from Sigma Aldrich, India. Chitin was purchased from India Sea Foods, Cochin and Sisal Fibers was purchased from Vibrant Nature, Chennai, India. Glutaraldehyde was procured from S.D. Fine Chemicals All chemicals used in the study are of analytical grade.

Preparation of chitin/starch/cellulose fiber blend with crosslinking agent glutaraldehyde

A known amount of chitin was dissolved in 5% CaCl₂ in methanol solution. Starch was mixed with minimum amount of water to make an emulsion. Chitin and starch solutions were mixed in different ratios with glutaraldehyde as crosslinking agent. Cellulose fiber was processed from sisal fiber by steam explosion method. The chitin starch blend solutions with glutaraldehyde were reinforced with modified Cellulose fibers in different proportions in the high speed mixer Remi India and then stored overnight. The blend was casted in plastic petri plates with the dimension 50cm × 50cm.

Batch experiments

Batch sorption experiments were carried out in temperature controlled orbit shaking machine by agitating 100 ml of tannery effluent using 1 g of CN/ST/CF+Glu blend adsorbent at fixed speed, 160 rpm for various time intervals. The extent of remediation of the effluent was investigated separately by changing the adsorbent dose and contact time in the range 1-6h and 1-6g. Effect of initial pH was studied by varying solution pH from 2 to 8 at the sorbent dosage of 1 g/100 ml for 1 h contact time. The pH of wastewater was adjusted by using 0.1 N HCl or 0.1 N NaOH.

After attaining the equilibrium the adsorbent was separated by filtration using filter paper and the residual concentration of the metals were estimated using Atomic absorption spectrophotometer (Varian AAA 220 FS).

Physico chemical analysis

The effluent from the textile industry has been collected in and around Ranipet industrial area. Various physico – chemical factors and metals were analysed for the samples as per the methods of APHA [12] including pH, electrical conductivity (EC), Total dissolved solids (TDS), Total hardness (TH), Total alkalinity (TA), content of chloride (Cl⁻), DO, BOD, COD concentration and heavy metal such as Cadmium, Chromium, Copper, Lead, Nickel, Zinc, concentration present in effluent are analyzed by atomic absorption spectroscopy.

RESULT AND DISCUSSION

The large numbers of textile industries release huge amount of effluents everyday without proper treatment [13] which adversely affect the aquatic systems [14,15,16], and the various physico-chemical parameters measured have values above the tolerable limits compared to the world health organization (WHO) standards even if the industries promise their treatment.

The various physico-chemical parameters measured from the textile effluent and there risks to the environment were discussed. The higher values of electrical conductivity impact on the taste of the water. There is an inverse correlation between the TDS and DO values. The higher value of TDS in the table causes negligible amount of DO in the effluent [17]. The higher values of alkalinity can strengthen the sodality soil conditions which will cause adverse effect in soil permeability [18]. The higher values of COD corresponds to the large amount of biologically resistant organic substances and the higher value of BOD indicates that only a negligible amount of oxygen is available for the organism in the effluent.

Effect of pH

The effect of pH is one of the significant parameter in adsorption process in which it can affect the active sites for metal ions adsorption on the surface of the adsorbent and the chemical form of the metallic species in aqueous solution [19]. To examine the effect of pH on the remediation efficiency, the pH was varied from 4.0 to 9.0. It was found that the reduction of physicochemical parameters and heavy metal ions were higher at acidic pH [20]. At low pH below 3, the amino ($\pm\text{NH}_2$) and hydroxyl ($\pm\text{OH}$) groups of chitin was protonated, and there is electrostatic

repulsion between the positive protons of the surface of chitin and NH_3^+ and H_3O^+ lead to decrease of adsorption capacity of metal ions [21]. When the pH is in the range of $3 < \text{pH} < 6$, the concentration of H_3O^+ ions decreases, which caused to expedite quickly and efficiently the adsorption of metal ions [22]. In the present investigation the optimum pH for adsorption was found to be 5 (Table – 1 and Figure – 1).

Table 1: Effect of pH on the treatment of Mixed effluent of Ranipet Industrial Area, India (CN+ST+CF)+GLU

Parameters	Raw effluent	pH					
		4	5	6	7	8	9
Electrical Conductivity ($\mu\text{mhos/cm}$)	2341	1023	958	322	216	140	96
DO mg/lit	0	0.65	4.5	2.4	3.22	3.92	4.5
BOD mg/lit	1165	601	41	191	325	554	825
COD mg/lit	3988	1531	90	422	854	1111	1221
TDS mg/lit	7288	3022	141	1642	2544	3750	3625
TSS mg/lit	697	314	51	129	185	285	375
TS mg/lit	2850	1147	94	285	445	710	920
Alkalinity mg/lit	1729	901	201	425	645	855	1451
Chloride mg/lit	1985	615	115	431	674	891	1212
Hardness mg/lit	9.5	3.2	1	3	4.3	5	6
Sodium mg/lit	1759	710	120	389	551	775	1125
Cadmium mg/lit	375	115	27	69	112	145	251
Chromium mg/lit	447	245	50	112	181	199	210
Copper mg/lit	416	200	44	95	110	151	214
Lead mg/lit	1065	610	121	245	396	425	516
Nickel mg/lit	416	35	120	187	225	245	344
Zinc mg/lit	1065	410	85	290	375	546	690

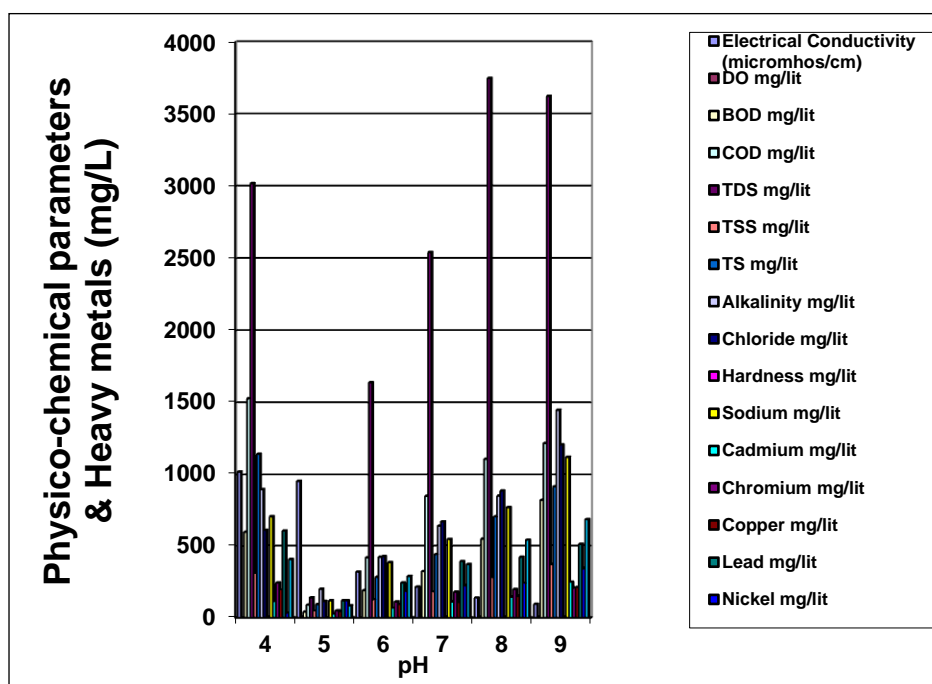


Figure 1: Effect of pH on the treatment of Mixed effluent of Ranipet Industrial Area, India (CN+ST+CF)+GLU

Effect of adsorbent dose

Table - 2 and Figure – 2 it is evident that the removal of pollutants from the effluent increases with the increase in the adsorbent dose. The reduction in various factors was very high initially when the adsorbent dosage was 1 g to 4g [23]. Further increment in the adsorbent dosage decreases the extent of remediation. Hence from the data it is

observed that the optimum adsorbent dosage was 4g/L and it is sufficient to remediate effectively the mixed effluent.

Table 2: Effect of adsorbent dose on the treatment of mixed effluent of Ranipet Industrial Area, India (CN+ST+CF) +GLU

Parameters	Raw effluent	Adsorbent dose					
		1 g	2 g	3 g	4 g	5g	6g
Electrical Conductivity (µmhos/cm)	2341	1121	720	395	295	210	110
DO mg/lit	0	0.31	1.1	2.11	2.94	3.72	4.4
BOD mg/lit	1165	610	415	285	135	105	45
COD mg/lit	3988	1525	910	420	220	123	110
TS mg/lit	7288	3110	1120	650	360	215	110
Alkalinity mg/lit	697	310	215	147	109	61	42
Chloride mg/lit	2850	1130	710	520	310	147	110
Hardness mg/lit	1729	910	615	320	211	135	101
Sodium mg/lit	1985	920	545	412	225	145	110
Cadmium mg/lit	9.5	6.2	3.1	2.4	1.4	1.1	0.7
Chromium mg/lit	1759	710	425	315	220	145	113
Copper mg/lit	375	110	86	65	41	28	12
Lead mg/lit	447	245	155	96	71	45	27
Nickel mg/lit	416	212	150	101	71	41	22
Zinc mg/lit	1065	610	325	245	195	112	101

Values expressed as mean of 6 individual values

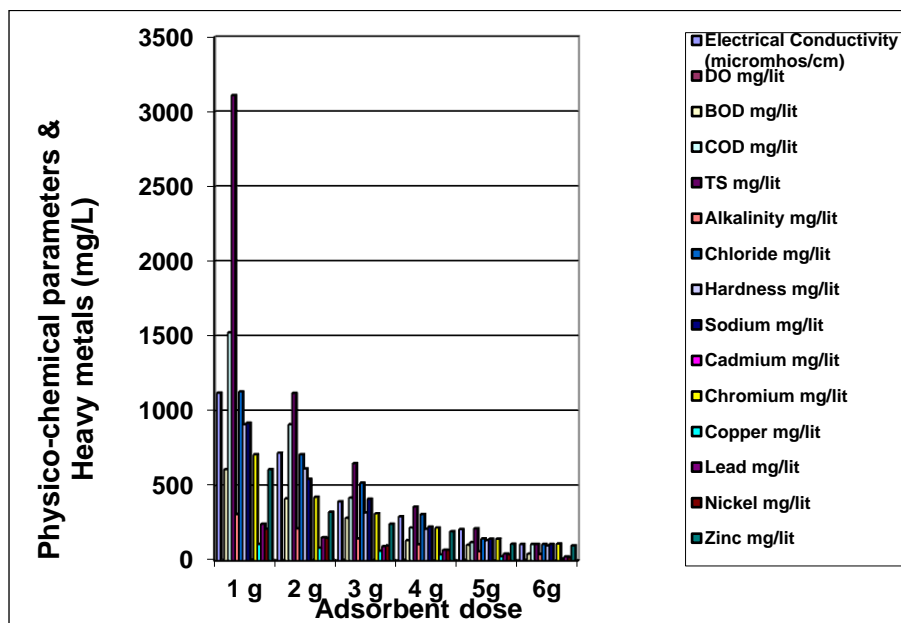


Figure 2: Effect of adsorbent dose on the treatment of Mixed effluent of Ranipet Industrial Area, India (CN+STARCH+CF) +GLU

Effect of contact time

Table 3 and Figure 3 represent the remediation levels of the mixed effluent with respect to the contact time. It is evident that the reduction of various parameters decreases with the increase in contact time of the effluent with the adsorbent. The rate of adsorption of pollutants increases rapidly when the contact time is 1 hour. Further increase in the contact time removes the pollutant slowly and reaches the equilibrium around 5 hour. The initial rapid phase of adsorption with time indicates that there are a large number of vacant sites and as a result there exists a concentration gradient between adsorbate in solution and adsorbate in the adsorbent surface [24]. As time precedes this concentration is reduced due to the accumulation of ions on the vacant sites and this causes a decrease in gradient in the adsorption rate after 5 hour.

Table 3: Effect of Contact time on the treatment of Mixed effluent of Ranipet Industrial Area, India (CN+ST+CF)+GLU

Parameters	Raw effluent	Contact time (Hrs)					
		1 Hr	2 Hr	3 Hr	4 Hr	5 Hr	6 Hr
Electrical Conductivity (µmhos/cm)	2341	1012	670	312	251	114	91
DO mg/lit	0	0.61	1.53	2.5	3.4	3.9	4.4
BOD mg/lit	1165	605	415	265	126	56	55
COD mg/lit	3988	1531	815	382	210	99	99
TS mg/lit	7288	3010	1022	510	320	150	145
Alkalinity mg/lit	697	311	210	120	75	50	50
Chloride mg/lit	2850	1147	670	415	285	112	110
Hardness mg/lit	1729	910	610	245	210	113	110
Sodium mg/lit	1985	812	603	401	212	113	112
Cadmium mg/lit	9.5	5.3	3	2	1.2	1	1
Chromium mg/lit	1759	701	401	300	201	112	110
Copper mg/lit	375	110	90	60	34	22	21
Lead mg/lit	447	221	151	91	67	35	30
Nickel mg/lit	416	201	112	80	61	31	20
Zinc mg/lit	1065	602	300	212	135	112	112

Values expressed as mean of 6 individual values

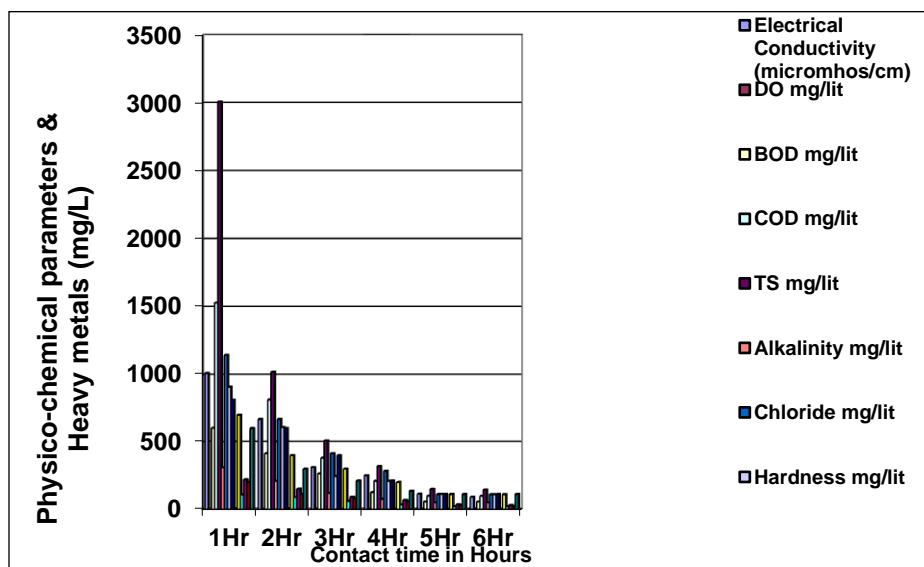


Figure 3: Effect of Contact time on the treatment of Mixed effluent of Ranipet Industrial Area, India (CN+ST+CF)+GLU

Sorption kinetics

The kinetics of metal ion adsorption onto the prepared ternary blend was determined with two different kinetic models i.e., the pseudo-first and pseudo-second order model. A good correlation of the kinetic data explains the adsorption mechanism of the metal ions on the solid phase [25].

Pseudo first order

The kinetics of adsorption of pseudo-first order equation was given by Lagergren. This was the first rate equation developed for sorption in liquid/solid systems [26].

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \text{-----(1)}$$

Where q_e and q_t are the amounts of metal adsorbed (mg/g) at equilibrium and at time t (min) and $k_1(\text{min}^{-1})$ is the adsorption rate constant of pseudo-first-order adsorption, respectively. A linear plot of $\log (q_e - q_t)$ against time

allows one to obtain the rate constant. From the graph the values of k_1 , q_e and R^2 was calculated and tabulated in Table 7.

Pseudo second order

The pseudo-second-order rate equation [27] can be represented as follows

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{-----(2)}$$

Where q_e and q_t are the amounts of metal adsorbed (mg/g) at equilibrium and at time t (min), k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the adsorption rate constant of pseudo second order adsorption. A linear plot of (t/q_t) versus t drawn for the pseudo-second-order model is shown in Fig. 9. From the graph the values of k_1 , q_e and R^2 was calculated and tabulated in table 7.

From these models the adsorption energy was normally portrayed by the Lagergren pseudo first demand model [28, 29]. At present the pseudo second demand model has been generally utilized for adsorption frameworks because of its great representation of the test information for a large portion of the adsorbent adsorbate frameworks.

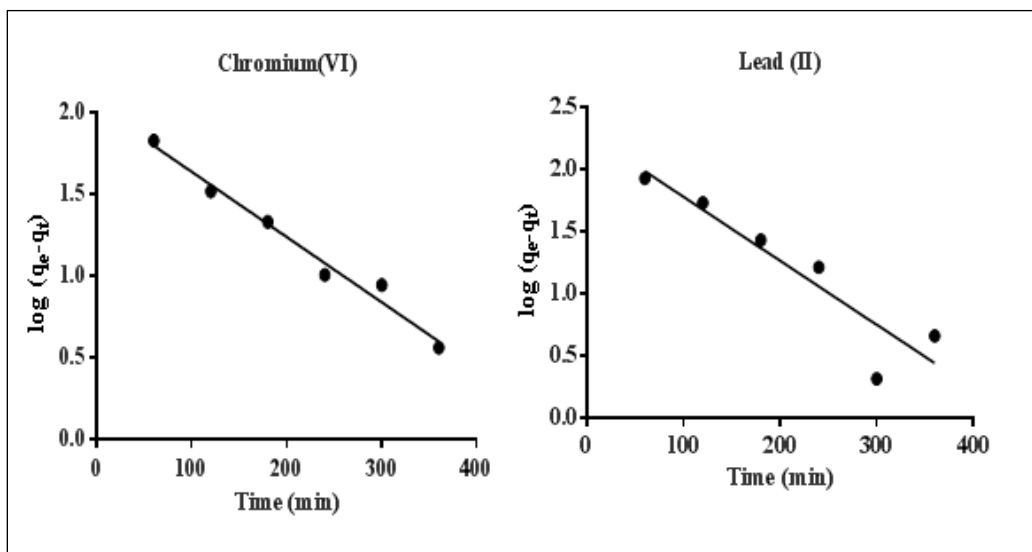


Figure 4: Pseudo-first-order sorption kinetic plot of (a) Chromium; (b) Lead

Table 4: Comparison between Lagergren pseudo-first-order and pseudo-second-order kinetic models for Cr(VI) and Pb(II) sorption by CN/ST/CF (1:1:1) - Glu

Metal ion	Pseudo-first-order kinetic model			Experimental value	Pseudo-second-order kinetic model		
	q_e (mg/g)	k_1 (min^{-1})	R^2		q_e (mg/g)	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
Cr(VI)	509.65	0.003991	0.9798	187.24	47.15	0.004691	0.9991
Pb(II)	445.5	0.005156	0.86	186.4	81.38	0.004346	0.9977

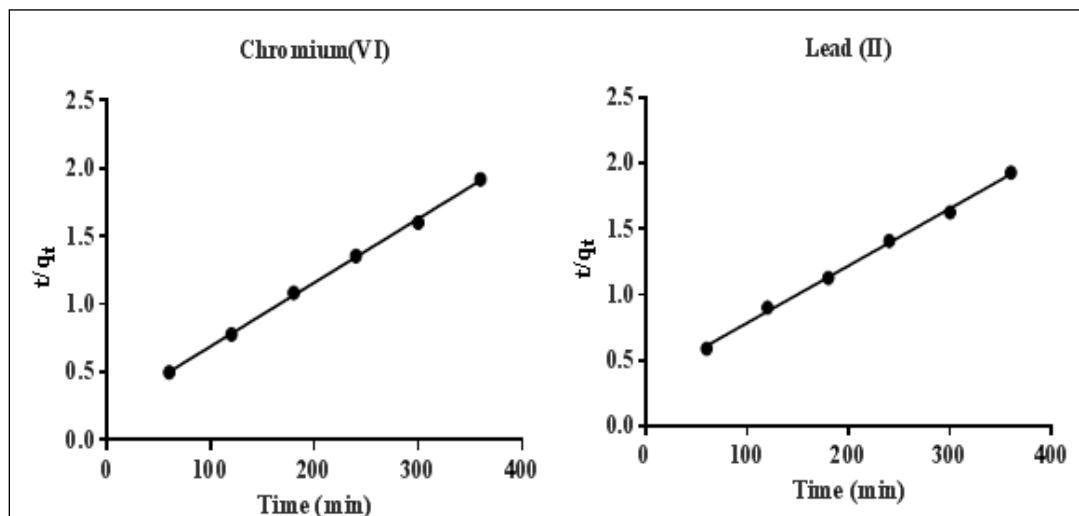


Figure 5: Pseudo-second-order sorption kinetic plot of (a) Chromium; (b) Lead

The linear plots of kinetic models pseudo first order and pseudo second order is represented in Fig 4 and Fig 5. From the linear plots the values of k_1 , k_2 , q_e and R^2 were calculated and tabulated in Table 4. The pseudo-second-order linear plots results higher R^2 values for both the heavy metal ions chromium and lead. Adsorption of Chromium and Lead onto CN/ST/CF (1:1:1) + Glu takes after pseudo second demand. The maximum adsorption of heavy metal on the surface of blend is due to the presence of nitrogen ions of chitin and $-OH$ gatherings of starch and cellulose are acknowledged as the principle receptive gatherings for heavy metal ions [30, 31].

CONCLUSION

The starch based blend was successfully prepared in the presence of crosslinking agent glutaraldehyde. The adsorption activity of prepared blend for the heavy metal and physico-chemical parameters were studied in terms of adsorption capacities, influencing of pH, contact time, and adsorbent dosage was also studied. The prepared blend was very effective for the adsorption of heavy metal and the physico-chemical parameters. The optimum pH value of the adsorbent was found to be 5. The optimum adsorbent dosage was found to be 4g. The effect of adsorption is maximum initially within 1hour of contact time. The equilibrium data for Cr (VI) and Pb(II) have been analyzed using Langmuir adsorption isotherm. The R^2 and R_L values for Cr (VI) and Pb (II) ions were calculated and found to be favorable. The kinetic mechanism for the adsorption of metal ions followed pseudo second- order model which provided the best experimental data correlation for this ions. This field of research hopes that starch based blend can be applied commercially instead of only laboratory scale for the removal of textile wastewater.

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