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Original Research Paper

Dechloridation of Treated Tannery Effluent by Using Leaves of Plants

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ABSTRACT

The present study deals with the dechloridation of treated tannery effluent by using plant leaves. The effluent after treatment, which is let out from the Common Tannery Effluent Treatment Plant (CETP) into Senkulum lake, Dindigul, Tamilnadu, was collected for the study. The physico-chemical characteristics of the treated tannery effluent were analysed. The pH value of effluent was 8.04, which slightly exceeded the recommended value. The electrical conductivity was 12,500 micromhos/cm, which was higher than the permissible limit. The value of hardness was 2210 mg/L. Out of the three cations tested, i.e. sodium, potassium and calcium, the sodium was 1275 mg/L followed by potassium (76mg/L) and calcium (295mg/L). The chloride content was higher (12,652 mg/L) in the tannery effluent. Leaves of plants such as *Cynodon dactylon, Psidium guajava, Azadirachta indica, Cassia tora* and *Cassia angustifolia* were used for the study. An adsorption kinetic study was performed with different weights of adsorbents (100-500 mg/100 mL), temperature (20-60°C) and pH (4-10), for chloride adsorption with different contact times (30 min, 1 hr, 2 hr). The *Cassia tora* leaves adsorbed maximum chloride compared to the leaves of other plants with a maximum weight of 200mg of adsorbent/100 mL, temperature of 40°C, pH 10 and contact time of 2 hours.

INTRODUCTION

India is one of the industrially developing countries in the world, and facing problems from negative impact of economic development due to industrial pollution. Rapid development of industrialization without adequate environmental safety measures has lead to pollution of waters. Every human society, whether urban, industrial or most technologically advanced, disposes certain kinds of byproducts and waste products into the biosphere in large quantities, ultimately affecting the normal functioning of ecosystems and having an adverse effect on plants, animals and human beings (Smith 1974). Industrial pollutants contaminate land surface by disposal of unwanted materials and discharge of effluents directly into the surrounding environment. One of the major industries that pollute the soil by discharging high amount of salt and chemicals, is tannery. The tannery industry is scattered unevenly in the country in large, medium, small and cottage sectors. The medium sector alone contributes about 60-70% of the total production and 20% of the exports of leather goods. A total of 2161 tanneries are located in India spreading across the states of Tamilnadu, West Bengal, Maharashtra, Punjab, Karnataka, Andhra Pradesh, Bihar and Uttar Pradesh. There are about 568 tanneries located in Tamilnadu among these. Dindigul is an important centre for leather processing with 61 tanneries. The minimum effluent produced during leather processing is 2500 to 5000 litres per 100 kg of hides. The effluent discharged from tanneries contains high pH, electrical conductivity, chlorides, sulphide, sulphate, carbonate, chromium, BOD, COD, oil and dyes (Apparao & Karthikeyan 1990). The tannery effluent form stagnant pools and seep through soil, and pollute drinking water and also the groundwater in a radius of about 6 km. In order to mitigate the problems posed by pollution from tanneries, a common effluent treatment plant has been established by the government of Tamilnadu in association with TALCO (Tamilnadu Leather Development Corporation) and Dindigul Tanner's Association. Even after the establishment of common effluent treatment plant, the treated effluent, which is stored in the Senkulam lake in the Dindigul-Batlagundu highway, is not suitable for agricultural purpose or surface irrigation (Rajan & Rukmani 2001). The soil of the whole area is already converted into alkaline soil due to addition of raw tannery effluent or treated tannery effluent containing high quantity of chloride. There is an urgent need to reduce chloride in the soil as well as in underground water. Many conventional methods like precipitation, evaporation, ion-exchange, reverse osmosis and electrodialysis are used for the removal of chloride. The main draw back of these technologies is lack of required treatment efficiency and cost effectiveness. Adsorption is the most attractive and cost effective technique for treating tannery effluent. Some locally available bioadsorbents such as leaves, seeds, stems, root and flowers of plants, agricultural wastes and charcoal have the capacity to adsorb chloride efficiently. The work related to the dechloridation of treated tannery effluent by using leaves of plants is totally wanting, hence, the present study was carried out.

MATERIALS AND METHODS

The polluted water samples were collected in 20-litre plastic containers from the Senkulum lake, Dindigul. After collection, the effluent water was immediately transported to the laboratory for analysis. The physico-chemical parameters such as pH, electrical conductivity, total solids, dissolved solids, suspended solids, total hardness, alkalinity, sodium, calcium, magnesium, sulphate, sulphide, carbonate, bicarbonate, phosphate, chloride, nitrogen, dissolved oxygen, carbon dioxide, BOD, COD and total chromium were analysed as per standard methods (APHA 1990). The tannery water was filtered through Whatman No. 1 filter paper before the analysis.

Leaves of plants such as *Cynodon dactylon, Psidium guajava, Azadirachta indica, Cassia tora* and *Cassia angustifola* were collected, washed, dried, powdered and sieved through 0.4 µm sieve (Kumar & Dara 1980).

Batch-type experiments were carried out for adsorption studies. 200 mg of adsorbent was weighed and 100 mL of tannery effluent was poured in a 250 mL clean conical flask, and kept in a mechanical shaker for a period of 2 hours. After 2 hours, the solution was filtered and estimated for chloride. Adsorption kinetic study was performed with varying contact times of 30-120 min, different weights of adsorbents 100-500 mg, temperature 20-60°C and pH 4-10.

The results obtained in various treatments were tested by analysis of variance (ANOVA) (Steel & Toorie 1960). The two-way ANOVA was conducted both within and between blocks to ascertain the effect of the control and different concentrations of the effluent on adsorption. The experimental data were statistically analysed by adapting the procedure described by Panse & Sukhatme (1957). Wherever the results were significant, the critical difference (CD) was worked out at 5% and 1% probability level.

Table 1: Physico-chemical characteristics of treated tannery effluent.

Parameters	Unit	Values	BIS standards
Colour		Dark brown	
Odour		Unpleasant	Unobjectionable
pH		8.04	6.5 to 8.5
Electrical conductivity	µmhos/cm	12,500	
Total Solids	mg/L	20,580	
Total dissolved solids	mg/L	20,260	500
Total suspended solids	mg/L	320	
Total hardness	mg/L	2210	300
Alkalinity	mg/L	225	200
Chloride	mg/L	12,652	250
Sulphate	mg/L	350.4	200
Sulphide	mg/L	5.4	
Carbonate	mg/L	ND	
Bicarbonate	mg/L	8.4	
Phosphate	mg/L	6.4	
Nitrogen	mg/L	0.912	
Dissolved carbon dioxide	mg/L	55.2	
Dissolved oxygen	mg/L	5.8	
BOD	mg/L	70.4	
COD	mg/L	530	
Sodium	mg/L	1275	
Potassium	mg/L	76	
Magnesium	mg/L	36	
Calcium	mg/L	295	
Total chromium	mg/L	0.012	0.05

All the values are average of ten replicates.

RESULTS AND DISCUSSION

The physico-chemical characteristics of the treated tannery effluent are presented in Table 1. The pH value of the effluent was 8.04, which was slightly higher than the recommended

Table 2: Adsorption of chloride from treated tannery effluent by leaves of different plants in relation to different contact times (constant weight 200 mg/100mL, pH 8 and Temperature 38°C).

S.No.	Name of Adsorbent	Initial chloride conc., mg/L	Contact Time ½ hr	1 hr	2 hr
1.	*Cynodon dactylon*		10684.2 ± 4.80 (15.6)	9981.1 ± 7.37 (21.1)	9078.2 ± 7.89 (28.2)
2.	*Psidium guajava*		11527.5 ± 6.34 (8.9)	11105.8 ± 4.14 (12.2)	10484.8 ±7.46 (17.1)
3.	*Azadirachta indica*	12652	11527.5 ± 6.28 (8.9)	11008.5 ± 7.89 (13)	10284.8 ±6.57 (18.7)
4.	*Cassia tora*		9516.3 ± 6.80 (24.8)	8891.4 ± 6.87 (29.7)	8012.4 ±7.65 (36.7)
5.	*Cassia augustifola*		9559.2 ± 5.44 (24.4)	8997.5 ± 6.74 (28.9)	8215.9 ±4.80 (35.1)

All the values are mean ± SD of five replicates; Mean percentage reduction of chloride is given in parentheses.

	SED	CD (0.05)	CD (0.01)
Adsorption	2.40091	4.80255 **	6.38737**
Contact time (h)	1.85973	3.72004**	4.94764 **
T vs h	4.15849	8.31826 **	11. 06326 **

** Significant at 0.05 and 0.01

Table 3: Adsorption of chloride from treated tannery effluent by leaves of different plants in relation to different weights (constant pH 8 and temperature 38°C with ½, 1 and 2 hour contact time).

Name of the Adsorbent	Initial Chloride Value mg/l	100mg/100ml	200mg/100ml	300mg/100ml	400mg/100ml	500 mg/100ml
½ Hour						
Cyanodon dactylon	12652	11246.4 ±4.49 (11.1)	10684.2±4.49 (15.6)	10121.7±6.49 (20)	9237.7±7.36 (26.7)	9559.4±7.17 (24.4)
Psidium guajava		12089.8 ± 7.12 (4.4)	11527.5±6.98 (8.9)	11104.8 ±6.01 (12.2)	10121.2±5.26 (20)	10682.8±6.37 (15.6)
Azadirachta indica		11949.3 ±7.01 (5.6)	11527.5±5.83 (8.9)	11107.4±5.77 (12.2)	10402.9±5.38 (17.8)	10689.4±6.50 (15.5)
Cassia tora		10110.4 ±5.50 (20)	9516.3±5.78 (24.8)	9152 ± 5.28 (27.7)	8399.4±7.40 (33.6)	8676.4±6.52 (31.4)
Cassia augustifola		10121.7 ±5.31 (20)	9559.4±6.73 (24.4)	9150 ± 7.09 (27.7)	8498.4±7.40 (32.8)	8711.4±6.38 (31.1)
1 Hour						
Cyanodon dactylon	12652	10543.5±5.56 (16.7)	9981.1±5.81 (21.1)	9408.8±7.12 (25.6)	8675.3±5.63 (31.4)	8856.5±6.59 (30)
Psidium guajava		11668.8±7.79 (7.8)	11105.8±6.22 (12.2)	10543.5±4.71 (16.7)	9740 ±5.83 (23)	10120.2±6.26 (20)
Azadirachta indica		11525.4±5.72 (8.9)	11008.5±7.41 (13)	10684.8±6.37 (15.5)	9992.4±6.73 (21)	10260.3±6.11 (18.9)
Cassia tora		9520.5±6.00 (24.8)	8891.4±5.54 (29.7)	8600.5±6.00 (32)	7921.4±5.41 (37.3)	8154.3±6.34 (35.5)
Cassia augustifola		9560.7±6.14 (24.4)	8997.5±6.00 (28.9)	8715.9±6.52 (31.1)	7918.4±5.45 (31.1)	8153.6±7.12 (35.4)
2 Hour						
Cyanodon dactylon	12652	9640.6±6.69 (23.8)	9078.2±7.12 (28.2)	8654.5±6.53 (31.6)	8052.6±5.77 (36.3)	8234.8±5.54 (34.9)
Psidium guajava		11186.9±7.02 (11.6)	10484.8±7.12 (17.1)	10060.2±6.34 (20.5)	9318.8±6.53 (26.3)	9550±6.89 (24.5)
Azadirachta indica		10806.5±6.81 (14.6)	10484.8±5.44 (17.1)	10064.3±4.84 (20.4)	9280.4±6.50 (26.1)	9552.4±6.06 (24.4)
Cassia tora		8702.4±5.31 (31.2)	8012.4±5.31 (36.7)	7689.4±6.50 (39.2)	7140.4±6.50 (43.6)	7392.4±7.09 (41.6)
Cassia augustifola		8698.4±6.87 (31.2)	8205.9±6.73 (35.1)	8082.5±6.65 (36)	7253.5±6.44 (42.7)	7572.4±5.72 (40)

All the values were Mean ± SD of five replicates. Percentage reduction of chloride was given in brackets

Hours		SED	CD (0.05)	CD (0.01)
½	Adsorption (t)	1.80271	3.57654**	4.73387**
	Different weight (h)	1.80271	3.57654**	4.73387**
	T vs h	4.0398	7.99738**	10.58526**
1	Adsorption (t)	1.75814	3.48810**	4.61682**
	Different weight (h)	1.75814	3.48810**	4.61682**
	T vs h	3.93131	7.79963**	10.32353**
2	Adsorption (t)	1.80142	3.57398**	4.73049**
	Different weight (h)	1.80142	3.57398**	4.73049**
	T vs h	4.02810	7.99167**	10.57770**

**** Significant at 0.05 and 0.01**

value. The electrical conductivity was 12,500 micromhos/ cm, which was also higher than the permissible limit. The tannery effluent contained 1275 mg/L sodium, 76mg/L potassium and 295mg/L calcium. The chloride content in the effluent was much higher at 12,652 mg/L. Rajan & Rukmani (2001) reported the physico-chemical characteristics of treated tannery effluent in Dindigul, which were similar to the result of the present study. Rani & Singaram (1996) reported that the tannery effluent with high load of sodium, chloride, sulphide, bicarbonate, chromium, ammonia with fats, dyes, acids and alkali contaminated surface and underground irrigation waters making them unsuitable for irrigation. Trivedi (1978) reported high concentration of chlorides in water indicating that the pollution is due to sewage as well as industrial waste. Even a moderate level of chloride can cause significant water pollution. Varadharajan et al. (1970) analysed tannery effluent and reported the presence of considerable amount of chlorides, carbonates, bicarbonates, sulphate, sodium and magnesium, which will pollute the land. Ahamed et al. (1977)

Table 4: Adsorption of chloride from Treated Tannery Effluent by Leaves of different plants in relation to different temperature (Constant weight 200mg/100ml and pH 8 with ½, 1 and 2 hour contact time).

Name of Adsorbent	Initial Chloride Value(mg/l)	20° C	40° C	60° C
½ Hour				
Cyanodon dactylon		11164.2 ±7.07 (11.8)	10684.2 ±6.87 (15.6)	11304.2 ±6.69 (10.7)
Psidium guajava		11981.4 ±6.59 (5.3)	11527.5 ±6.10 (8.9)	12170.2 ±6.45 (3.8)
Azadirachta indica	12652	11983.4 ±6.03 (5.3)	11527.5 ±6.10 (8.9)	12206.4 ±6.88 (3.5)
Cassia tora		9960.2 ±5.78 (21.2)	9516.3 ±6.11 (24.8)	10216.3 ±6.33 (19.3)
Cassia augustifola		9910.3 ±6.44 (21.7)	9559.5 ±6.13 (24.4)	10401.4 ±6.14 (17.8)
1 Hour				
Cyanodon dactylon		10471.6 ±6.69 (17.2)	9981.1 ±6.14 (21.1)	10601.2 ±5.80 (16.2)
Psidium guajava		11682.4 ±6.18 (7.7)	11105.6 ±7.89 (12.2)	11870.4 ±6.50 (6.2)
Azadirachta indica	12652	11428.3 ±6.11 (9.7)	11008.5 ±7.41 (13)	11686.3 ±6.30 (7.6)
Cassia tora		9342.8 ±5.26 (26.2)	8891.4 ±5.68 (29.7)	9543.4 ±6.18 (24.6)
Cassia augustifola		9454.2 ±5.63 (25.3)	8992.5 ± 6.14 (28.9)	9620.5 ± 6.40 (24)
2 Hour				
Cyanodon dactylon		11987.5 ±5.72 (5.2)	11526.4 ±6.10 (8.9)	12147.5 ±6.59 (4)
Psidium guajava		11682.4 ±6.18 (7.7)	11260.4 ±5.94 (11)	11942.4 ±6.10 (5.6)
Azadirachta indica	12652	11814.4 ±6.10 (6.7)	11189.4 ±7.23 (11.6)	11924.6 ±8.81 (5.7)
Cassia tora		9984.4 ±6.10 (21.9)	9559.4 ±6.69 (24.4)	10328.6 ±6.06 (18.4)
Cassia augustifola		10968.5 ±6.46 (13.3)	10543.5 ±6.06 (16.7)	11267.8 ±6.14 (11)

All the values were Mean ± SD of five replicates. Percentage reduction of chloride was given in brackets

Hours		SED	CD (0.05)	CD (0.01)
½	Adsorption (t)	2.33532	4.67136**	6.21289**
	Different temperature (h)	1.80893	3.61842**	4.81249**
	T vs h	4.04490	8.09103**	10.76105**
1	Adsorption (t)	2.09032	4.18281**	6.86310**
	Different temperature (h)	1.49214	3.58596**	4.61129**
	T vs h	3.48080	7.56534**	10.67184**
2	Adsorption (t)	2.27635	4.55340**	6.05601**
	Different temperature (h)	1.76325	3.52705**	4.69096**
	T vs h	3.94276	7.88672**	10.48931**

** Significant at 0.05 and 0.01

conducted a survey of the tannery affected areas of North Arcot District of Tamilnadu and observed that the total soluble salts and chloride values of surface water in the river at Vaniyambodi were about 2000 and 800 mg/L respectively.

Adsorption of chloride from treated tannery effluent by leaves of different plants in relation to different contact times (½, 1 and 2 hours) is given in Table 2. Among the different plants *Cassia tora* leaves adsorbed maximum chloride

Table 5: Adsorption of chloride from treated tannery effluent by leaves of different plants in relation to different pH (Constant weight 200mg/100mL and Temp.38° C with ½, 1 and 2 hour contact time).

Name of Adsorbent	Initial Chloride Value(mg/l)	pH 4	pH 6	pH 8	pH 10
½ Hour					
Cyanodon dactylon		11246.4 ±6.10 (11.1)	11164.2 ±6.05 (11.8)	10684.2 ±6.37 (15.6)	10121.7 ±6.07 (20)
Psidium guajava		12089.8 ±6.97 (4.4)	11981.4 ±5.54 (5.3)	11527.5 ±6.0 (8.9)	11104.8 ±6.79 (12.2)
Azadirachta indica	12652	11949.3 ±6.79 (5.6)	11983.4 ±5.85 (5.3)	11527.5 ±6.0 (8.9)	11107.4 ±6.18 (12.2)
Cassia tora		10110.4 ±6.38 (20.1)	9960.2 ±6.18 (21.3)	9516.3 ±6.07 (24.7)	9150.3 ±6.41 (27.6)
Cassia augustifola		10121.7 ±6.07 (20)	9910.3 ±6.07 (21.6)	9559.4 ±7.23 (24.4)	9250.4 ±6.26 (26.9)
1 Hour					
Cyanodon dactylon		10543.5 ±6.24 (16.7)	10471.6 ±5.68 (17.2)	9981.1 ±6.12 (21.1)	9408.8 ±6.37 (25.6)
Psidium guajava		11668.8 ±6.53 (7.8)	11482.4 ±6.06 (9.2)	11105.8 ±6.41 (12.2)	10543.5 ±5.95 (16.7)
Azadirachta indica	12652	11525.4 ±5.41 (8.9)	11428.3 ±6.18 (9.7)	11008.5 ±6.20 (12.2)	10684.8 ±6.30 (15.5)
Cassia tora		9520.5 ±5.95 (24.8)	9342.8 ±6.09 (26.2)	8891.4 ±5.85 (29.7)	8600.5 ±6.20 (32)
Cassia augustifola		9560.7 ±6.53 (24.4)	9454.2 ±6.05 (25.3)	8997.5 ±5.74 (28.9)	8715.9 ±5.72 (31.1)
2 Hour					
Cyanodon dactylon		9640.6 ±5.98 (23.8)	9538.2 ±6.09 (24.6)	9078.2 ±5.93 (28.2)	8654.5 ±6.14 (31.6)
Psidium guajava		11186.9 ±5.87 (11.6)	10892.5 ±5.93 (13.9)	10484.8 ±6.30 (17.1)	10060.2 ±6.37 (20.5)
Azadirachta indica	12652	10806.5 ±6.38 (14.6)	10573.6 ±5.63 (16.4)	10484.8 ±5.97 (17.1)	10064.3 ±6.18 (20.5)
Cassia tora		8702.4 ±6.18 (31.2)	8389.3 ±6.68 (33.7)	8012.4 ±6.06 (36.7)	7689.4 ±6.06 (39.2)
Cassia augustifola		8698.4 ±7.40 (31.2)	8489.5 ±7.41 (32.9)	8205.9 ±6.34 (35.1)	8092.4 ±5.94 (36)

All the values were Mean ± SD of five replicates. Percentage reduction of chloride was given in brackets

Hours		SED	CD (0.05)	CD (0.01)
½	Adsorption (t)	1.94268	3.86615**	5.12989**
	Different pH (h)	1.73758	3.45799**	4.58831**
	T vs h	3.88536	7.73230**	10.25977**
1	Adsorption (t)	1.92633	3.83361**	5.08672**
	Different pH (h)	1.72296	3.42889**	4.54970**
	T vs h	3.85266	7.66723**	10.17343**
2	Adsorption (t)	1.98431	3.94901**	5.23983**
	Different pH (h)	1.77482	3.53210**	4.68664**
	T vs h	3.96863	7.89801**	10.47966**

**** Significant at 0.05 and 0.01**

(36.7%) compared to the leaves of other plants with a maximum contact time of 2 hours. The minimum adsorption at 2 hrs was reported for *Psidium guajava* (17.1%). A similar observation was reported by Deo & Ali (1993a, b). The effectiveness of adsorbent was tested under various conditions involving change in contact time. Bulut & Sal (2006) reported that the maximum removal of Pb(II) was attained after 60 min of stirring time for the removal of lead by wheat bran from the wastewater. In the present study the maximum adsorption of chloride is at 2 hrs contact time, so using a contact time of not beyond 2 hrs reduce the chloride content from treated tannery effluent. Adsorption of chloride

from treated tannery effluent by leaves of different plants in relation to different weights with constant pH of 8 and temperature of 38°C with ½, 1 and 2 hours of contact time is presented in Table 3. Among the different plants, *Cassia tora* leaves adsorbed maximum chloride (33.6, 37.36 and 43.6% for ½, 1 and 2 hours respectively) compared to the leaves of other plants with a maximum of 400 mg weight of adsorbent. The minimum adsorption at 400 mg was reported for *Azadirachta indica*. In a similar adsorption experiment, Deo & Ali (1993a) reported that 20 mg/L of the bioadsorbent was very effective. However, at high concentration a declining trend was observed. Similar result was found in the present study when the adsorbent weight was increased. Srivastava et al. (2002) reported that the removal of Mn^{2+} was dependent on the adsorbent dose. Adsorption of chloride from treated tannery effluent by leaves of different plants in relation to different temperature with constant pH and weight of adsorbent 200 mg in ½, 1 and 2 hours of contact time is presented in Table 4. Among the different plants *Cassia tora* leaves adsorbed maximum chloride compared to the leaves of other plants with a maximum temperature of 40°C in different contact time. The minimum adsorption at 40°C was reported for *Psidium guajava*. Similar adsorption experiments showed that the effect of temperature on the removal of Pb^{2+} and Cd^{2+} in aqueous solution by *C. bicolor* biomass with varying temperatures between 30 and 80°C. The adsorption of metal ion by the *C. bicolor* biomass increased with increase in temperature, which is typical for the biosorption of most metal ions from their solutions. However, the magnitude of such increase continues to decline as temperature increases from 30 to 80°C. This is because with increasing temperature, the attractive forces between biomass surface and metal ions are weakened and the sorption decreases. Careful examination of the data revealed that most of the metal ions were removed between the temperatures of 30 and 50°C (Manju et al. 1998). Adsorption of chloride from treated tannery effluent by leaves of different plants in relation to different pH with weight of adsorbent 200 mg and temperature 38°C in ½, 1 and 2 hours of contact time is presented in Table 5. Among the different plants *Cassia tora* leaves adsorbed maximum chloride, with maximum pH of 10. The minimum adsorption at pH 10 was reported for *Azadirachta indica* in different contact times. Similar adsorption experiments showed a higher adsorption percentage of the removal of chromium from synthetic effluent by using leaf powder at a pH of 1.55. A fall in adsorption with increasing pH may be due to deprotonation. Srivastava et al. (1996) conducted kinetic studies at pH 5.0 for Cu(II), at pH 6.0 for Cr (VI) and Pb (II), and pH 8.0 for Ni (II). Saravanane et al. (2002) found that the uptake of Cr^{6+}, Ni^{2+} and Pb^{2+} ions is function of hydrogen ion concentration over a pH range of 2-12 at solution ion concentration of 0.1g/L. King et al. (2008) reported that pH is an important parameter for the removal of zinc ions from aqueous solutions by the biomass of *Azadirachta indica* bark having a high content of ionizable groups on the cell wall polysaccharides, which makes it very liable to the influence of the pH. The adsorption was observed to increase with increase in pH.

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