

Chromium(VI) Removal by Fe(III)-loaded Succinylated Mercerized Cellulose from Aqueous Solution

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A new chelating material from mercerized cotton linter was prepared by a reaction with succinic anhydride in the presence of toluene/triethylamine and a 4-dimethylaminopyridine catalyst, followed by reacting with Fe(III) to obtain the final product. The materials were characterized by Fourier transform infrared spectrometry, scanning electron microscopy, and energy dispersive spectrometer; the adsorption of chromium(VI) from an aqueous solution was examined. The Langmuir isotherm accurately fit the experimental data, and the calculated adsorption ability of Fe(III)-loaded adsorbent for chromium(VI) was 11.1 mg/g. The adsorption process followed a pseudo-second-order kinetic model.

Keywords: Adsorption; Chromium(VI); Fe(III)-loaded adsorbent

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INTRODUCTION

Chromium is discharged from multiple industries such as leather tanning, textiles, and photography. Chromium(VI) is a hazardous heavy metal, and long- or short-term contact or inhalation results in carcinogenicity. Furthermore, it is consistently dangerous for the environment. Therefore, removing or reducing chromium(VI) from wastewater before its emission into the environment is critical. A variety of chemical treatment techniques have been investigated and applied. The removal of pollutants from effluents is commonly conducted by ion exchange, absorption, reduction, and precipitation (Gurgel *et al.* 2009). However, the use of costly chemicals and poor removal capacity limit the application of these treatments (Park *et al.* 2005; Park *et al.* 2007). Therefore, researchers have investigated a variety of sorbents for the removal of chromium(VI) from water (Bai and Deng 2004; Mohanty *et al.* 2005; Abdel-Halim *et al.* 2006; Park *et al.* 2006a,b; Zubair *et al.* 2008; Zhang *et al.* 2008; Gurgel *et al.* 2009; Lo and Mak 2011).

Activated carbon can be obtained from a variety of materials such as wood, industrial waste, and coal, and it is an effective material for removing chromium(VI) in effluents. However, some adsorbents exhibit poor or slow adsorption and high cost. Hence, the exploration of high-efficiency adsorbents is imperative (Namasivayam and Sureshkumar 2008). A number of metal-loading materials that remove pollutants from water have been reported. These include yttrium-loaded poly-(hydroxamic acid) resin (Haron *et al.* 1995), polymer complex of zirconium(V) (Yuchi *et al.* 1999), Fe(III)-loaded cotton cellulose (Zhao *et al.* 2008), chitosan-Fe(III) complex (Zimmermann *et al.* 2010; Shen *et al.* 2013), crosslinked alumina-chitosan hybrid adsorbent (Ji *et al.* 2012), and chitosan/Al₂O₃/magnetite nanoparticles composite adsorbent (Bahareh *et al.* 2015).

In this study Fe(III)-loaded succinylated mercerized cellulose was used to remove chromium(VI) from water. The availability of a low cost and biodegradable carrier,

cotton linter, together with the use of an environmentally safe and low cost metal, iron, facilitated this work. A simple preparation procedure and easy regeneration and reuse further enhanced our interest in choosing this content for our research. To obtain this adsorbent, mercerized cotton linter (MC) was reacted with succinic anhydride (SA), and succinylated mercerized cotton linter (SMC) was reacted with Fe(III) solution to obtain Fe-functionalized succinylated mercerized cotton linter (ISMC). The absorption of chromium(VI) by ISMC was described by the Langmuir model. Fourier transform infrared spectrometry (FTIR), scanning electron microscopy (SEM), and energy dispersive spectrometer (EDS) were used to characterize the product.

EXPERIMENTAL

Materials

Analytical grade chemicals were purchased from Damao, China. $K_2Cr_2O_7$ powder was dissolved in deionized water to obtain a chromium working solution of 30 mg $Cr_2O_7^{2-}$ /L. The Fe(III) solution (0.2 mol/L) was obtained by dissolving $FeCl_3 \cdot 6H_2O$ into a sodium acetate-acetic acid buffer (pH 4.5).

Preparation of Modified Cotton Linter

Preparation of mercerized cotton linter

Cotton linter was manually cut into small pieces and treated with 15 wt.% NaOH at room temperature for 24 h. The mercerized cotton linter was filtered and washed with deionized water until it reached neutral pH. MC was subsequently treated with acetone at room temperature for 3 h, washed, and dried at 30 °C in a vacuum drier for 12 h.

Preparation of SMC

Five grams of MC were immersed in 160 mL of toluene/triethylamine (70/30, w/w) in a flask. Under constant stirring and refluxing, the temperature was raised to 130 °C, and then 11.70 g of SA and 0.42 g of 4-dimethylaminopyridine were added to the mixture under N_2 atmosphere with stirring and refluxing for 12 h. The mixture was cooled, and extra SA was removed by Soxhlet extraction using tetrahydrofuran/ethanol (50/50 v/v) for 10 h. To achieve a better chelating, the carboxylate groups were modified (Gurgel *et al.* 2009). The SMC was placed in $NaHCO_3$ solution for 30 min, filtered, and washed with ethanol. Finally, the SMC was vacuum-dried at 30 °C for 12 h.

Preparation of ISMC

Five grams of SMC was stirred with 200 mL of Fe(III) (0.2 mol/L) at 25 °C for 24 h. Subsequently, the ISMC was washed with deionized water to eliminate unloaded Fe(III) and then vacuum-dried at 60 °C for 12 h.

Characterization of the Material

The degree of succinylation of SMC was determined by measuring the introduced carboxylic acid groups (Gurgel *et al.* 2008). Briefly, 0.10 g of SMC was immersed in 80 mL of NaOH (0.01 mol/L) and stirred for 30 min. The mixture was filtered, and 20 mL of filtrate was titrated with HCl (0.01 mol/L) in three parallel titrations (Karnitz *et al.* 2007). The carboxyl functional groups were calculated according to Eq. (1):

$$C_{COOH} = \left[\frac{(C_1 \times V_1/4) - (C_2 \times V_2)}{m/4} \right] \quad (1)$$

where C_1 and C_2 are the concentrations of NaOH and HCl solutions, respectively, V_1 is the volume of NaOH, V_2 is the volume of HCl consumed by the unreacted base, and m is the mass of SMC.

A specific amount of ISMC was placed into a beaker with 2 mol/L HCl to determine the content of loaded Fe(III), and then the content of Fe(III) in the filtrate was determined using an atomic absorption spectrophotometer.

FTIR spectra were recorded on an instrument (IRPretige-21, Shimadzu, Japan) with scanning from 400 to 4000 cm^{-1} wave numbers.

SEM and EDS were obtained by an FEI Quanta-200 environmental scanning electron microscope combined with an EDS operating at 5 kV accelerating voltage. The samples were sputtered with gold prior to analysis.

Batch Sorption Experiments

To determine the influence of pH, 100 mg of ISMC was put into a 250-mL beaker containing 50 mL of 30 mg $\text{Cr}_2\text{O}_7^{2-}/\text{L}$ ion solution. The pH range was 2 to 8. During adsorption, NaOH and HCl solutions (0.1 mol/L) were used to adjust the pH, and the beakers were stirred continuously for 90 min at 25 °C.

Kinetic studies were performed in a 500-mL beaker flask with 500 mL of 30 to 100 mg $\text{Cr}_2\text{O}_7^{2-}/\text{L}$ solution at room temperature. A total of 1.00 g of ISMC was added, and the flask constantly stirred. A small amount (4 mL) of sample was filtered out at desired time intervals to analyze the chromium(VI) ion concentration. NaOH and HCl solutions (0.1 mol/L) were used to maintain the initial pH of 2. The experiments were performed at 298 K. In the equilibrium experiments, 0.10 g of ISMC was placed into beakers containing 50 mL of chromium(VI) solution at different concentrations. The beakers were stirred for 90 min at room temperature. The initial pH of 2 was maintained throughout the experiment.

Regeneration and reuse of the adsorbent

For the regeneration, 0.10 g of ISMC saturated with chromium(VI) was put into 50 mL of 1 mol/L NaOH aqueous and stirred for 1 h. The chromium(VI) concentration was determined. The adsorbent was then washed with deionized water to remove the extra of NaOH and recondition the adsorbent. This procedure was repeated four times for each absorption/regeneration cycle.

RESULTS AND DISCUSSION

Degree of Succinylation and Iron(III)

The modified material was synthesized as described above. The degree of succinylation was 2.9 mmol/g, and 72 mg/g Iron(III) was loaded onto ISMC.

FTIR Analysis

FTIR spectra from of MC and SMC are shown in Fig. 1. The peaks at 3375, 2895, 1375, 1158, and 1058 cm^{-1} are related to pure cotton linter. O–H stretching was

represented by the band at 3375 cm^{-1} , and the peak at 2895 cm^{-1} was assigned to C–H stretching. The band at 1375 cm^{-1} was associated with O–H bending. The peak at 1158 cm^{-1} represented C–O antisymmetric bridge stretching (Liu *et al.* 2011). The new band at 1732 cm^{-1} in the SMC spectrum illustrated that an esterification reaction occurred between the cotton linter and SA. Furthermore, the peaks at 1417 and 1573 cm^{-1} were associated with symmetric and asymmetric stretching vibrations of the ionic carboxylic groups, which proved that the first modification was successful (Sanna *et al.* 2013).

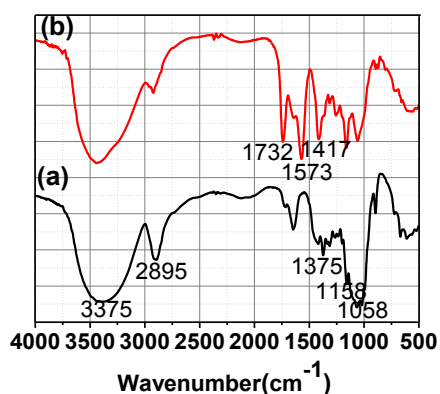


Fig. 1. FTIR analysis of (a) MC and (b) SMC

SEM and EDS Analysis

SEM images of MC and ISMC are shown in Fig. 2. Compared with ISMC, the surface of the raw material was smoother. After modification, the surface of the product became rough compared to the raw material. These observations indicated that the modification process changed the structure of the cellulose surface and that iron was loaded onto the surface of ISMC.

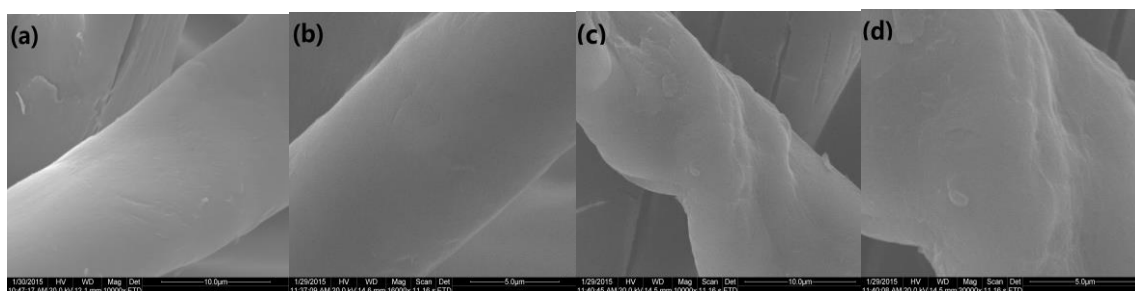


Fig. 2. SEM surface analysis of (a, b) MC and (c, d) ISMC

To further confirm the loading of Fe(III) and the adsorption of chromium(VI) onto ISMC, EDS spectra were generated (Fig. 3). The surface of the samples detected corresponding signal peaks. As expected, the main elements in MC were C and O (Fig. 3(a)), which were also observed in the other materials (Albadarin *et al.* 2013). In contrast, new Fe peaks were found in ISMC samples (Fig. 3(b,c)). These observations showed that Fe(III) was loaded onto the surface of ISMC (Cai *et al.* 2015). Furthermore, new Cr peaks were present in the ISMC samples that had absorbed chromium(VI). This observation indicated that chromium(VI) was absorbed onto ISMC.

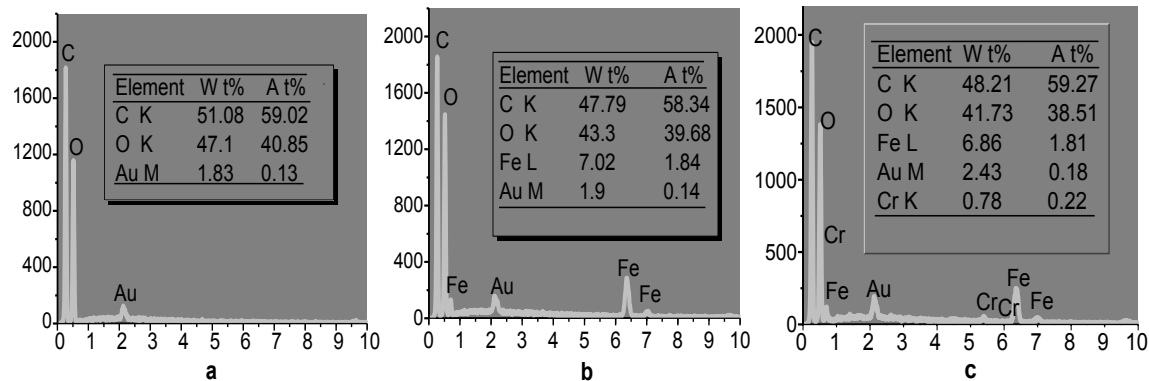


Fig. 3. EDS surface analysis of (a) MC, (b) ISMC, and (c) ISMC after adsorption

Effect of pH on Absorption

Chromium(VI) exists in different forms in water, including H_2CrO_4 , HCr_2O_7^- , CrO_4^{2-} , HCrO_4^- , and $\text{Cr}_2\text{O}_7^{2-}$. From pH 2 to 6, HCrO_4^- , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$ are present, but HCrO_4^- predominates. At higher pH, CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ begin to dominate. CrO_4^{2-} is the only aqueous chromate when the pH is higher than 7.5 (Mallick *et al.* 2006).

In acidic solution, iron dissolved from ISMC, and the concentration of dissolved iron decreased with increasing pH. While the amount of dissolved iron was less than 2% of ISMC, so the effect of this aspect could be ignored.

The adsorption capacities were lower at higher pH. The optimum pH was 2. At lower pH values, the main form of chromium(VI) was HCrO_4^- , which requires one exchange site. As pH increased, the increase in CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$, which require two exchange sites, resulted in the decreased adsorption of chromium(VI) (Leandro *et al.* 2009). In addition, the increase of OH^- , which could be a competitive adsorption ion for chromium(VI), also reduced the adsorption of chromium(VI). Therefore, the optimum pH was used in all subsequent experiments.

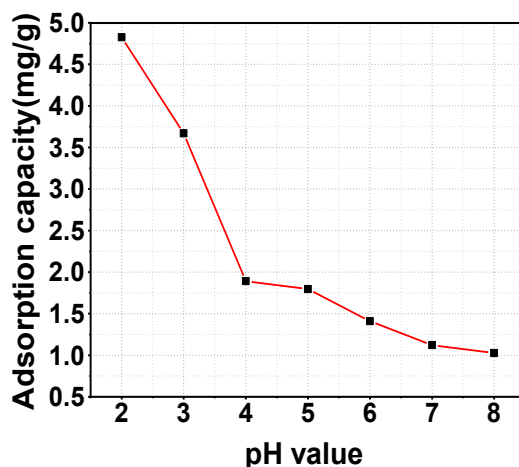


Fig. 4. Effect of pH on the adsorption of chromium(VI) by ISMC

Adsorption Kinetics

Adsorption kinetic models, based on evaluation of the rate of adsorption, were used to calculate the optimum adsorption time. The experiments were performed after 180 min to ensure that full equilibrium was achieved. Figure 5(a) shows that the

absorption ability increased rapidly in the initial 15 min and then increased slowly. ISMC rapidly removed chromium(VI) from the solution; absorption potentially occurred on the ISMC surface (Zhao *et al.* 2009). After 90 min, the absorption capacity was stable, so 90 min was considered the optimum adsorption time.

The pseudo-first-order kinetic model can be expressed by Eq. 2:

$$\lg(q_e - q_t) = \lg q_e - k_1 t \quad (2)$$

where k_1 is the constant and q_t and q_e are the amounts of adsorbed chromium(VI) on ISMC at time t and equilibrium, respectively. The pseudo-second-order kinetic model is expressed by Eq. 3, where k_2 is a constant.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

The intraparticle diffusion model can be defined by Eq. 4, where k_i is the constant and C is a constant corresponding to the strength of the boundary layer.

$$q_t = k_i t^{1/2} + C \quad (4)$$

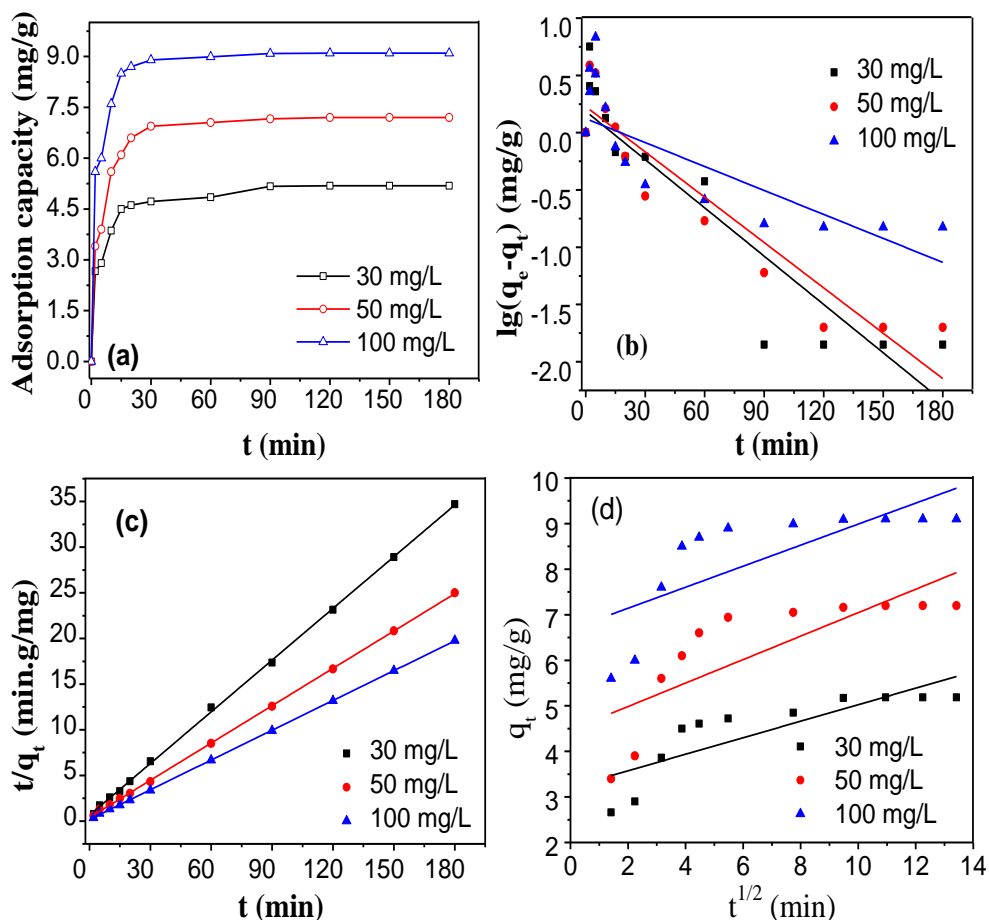


Fig. 5. (a) Kinetic models for chromium(VI) adsorption onto ISMC, (b) pseudo-first-order kinetic plot, (c) pseudo-second-order kinetic plot, and (d) intraparticle diffusion model

The pseudo-second-order model gave the best correlation with the experimental data (Wu *et al.* 2009). The $q_{e,cal}$ represents the amount of chromium(VI) adsorbed at equilibrium time. As shown in Table 1, the calculated $q_{e,cal}$ in the pseudo-second-order model agreed most closely with the experimentally obtained $q_{e,exp}$. Also, the correlation coefficient (R^2) was close to 1.0. Therefore, the absorption of chromium(VI) onto ISMC followed a pseudo-second-order kinetic model.

Table 1. Parameters of Kinetic Models

Cr(VI) Concentration (mg/L)	$q_{e,exp}$	Pseudo-first-order			Pseudo-second-order			Intraparticle Diffusion Model		
		k_1	$q_{e,cal}$	R^2	k_2	$q_{e,cal}$	R^2	k_i	C	R^2
30	5.2	0.0146	6.5	0.856	0.0554	5.3	0.996	0.183	3.21	0.666
50	7.2	0.0132	9.8	0.874	0.0500	7.3	0.998	0.256	4.47	0.583
100	9.1	0.0070	3.4	0.647	0.0712	9.2	0.999	0.231	6.68	0.522

Adsorption Isotherms

Adsorption isotherms are essential for understanding the nature of the interactions between the adsorbent and the concentration of the adsorbate (Bhatnagar *et al.* 2011). The absorption ability and removal efficiency of ISMC were studied in different chromium(VI) concentrations (Fig. 6(a)). Initially, absorption increased as the chromium(VI) concentration increased, with a high rate at lower concentrations. However, removal efficiency decreased from 71% to 27% at higher initial concentrations.

The Langmuir and Freundlich isotherm equations are typical two-parameter theoretical models evaluate absorption. The Langmuir model is for physical absorption processes, while the Freundlich model represents chemical adsorption. The Langmuir and Freundlich isotherm models are linearly expressed in Eq. 5 and 6, respectively,

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \quad (5)$$

$$\lg q_e = \lg k + \frac{1}{n} \lg c_e \quad (6)$$

where q_e is the equilibrium absorption ability, and k and $1/n$ represent absorption ability and strength, respectively. q_{max} is the maximum absorption ability, C_e is the content of chromium(VI) at equilibrium time, and b is the Langmuir constant. The variable k is the Freundlich constant. The standard deviation (S. D.) was determined as follows,

$$S.D. = \sqrt{\frac{\sum [(Q_{e,exp} - Q_{e,cal})/Q_{e,exp}]^2}{4}} \quad (7)$$

where $Q_{e,exp}$ and $Q_{e,cal}$ are the experimental and calculated data, respectively.

The results are shown in Fig. 6(b) and Table 2. The Freundlich model ($R^2 = 0.9911$, $x^2 = 0.023$) and the Langmuir model ($R^2 = 0.9994$, $x^2 = 0.0053$) both effectively described the absorption of chromium(VI) onto ISMC. Comparatively speaking, the latter was more suitable, which suggests that chromium(VI) is absorbed as a monolayer surface.

Fitting to this model indicates that the active sites of the loaded adsorbent play a vital role in the adsorption of chromium(VI).

The maximum absorption ability (q_{max}) obtained from Eq. 5 was 11.1 mg/g. The value for parameter b (< 1) indicated that these adsorbents had a high chromium(VI) affinity. The Freundlich adsorption intensity parameter (n) was 2.445, indicating the applicability of the Freundlich isotherm and the favorable adsorption of chromium(VI).

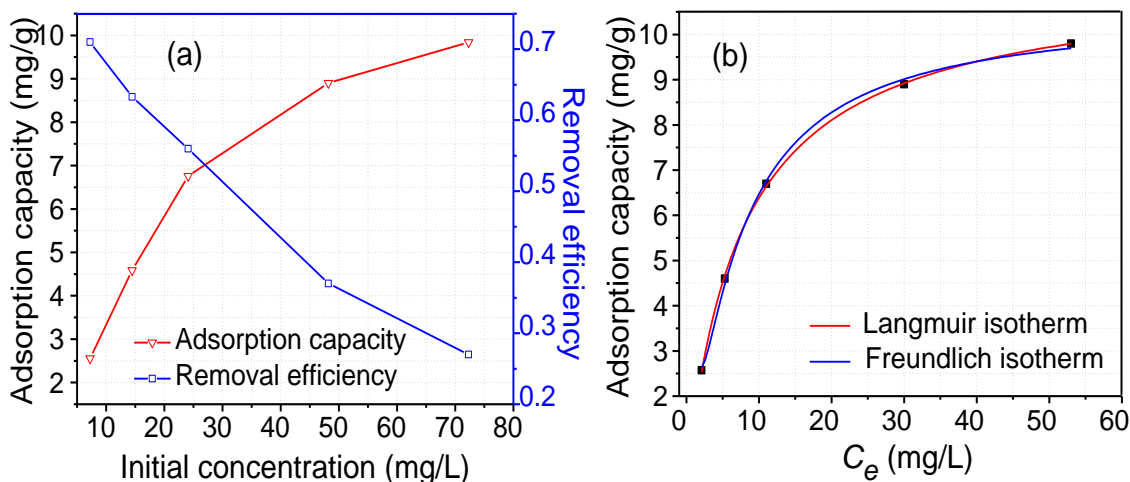


Fig. 6. Adsorption isotherms for the absorption of chromium(VI) onto ISMC

Table 2. Isotherm Parameters for the Adsorption of Chromium(VI) onto ISMC

q_{max}	Langmuir Isotherm					Freundlich Isotherm				
	b	R^2	X^2	$S.D.$	n	k	R^2	X^2	$S.D.$	
11.1	0.13722	0.9994	0.0053	1.142	2.445	5.929	0.9911	0.023	2.110	

Desorption

The regeneration of the adsorbent is important in the practical application. Figure 7 shows the results of chromium(VI) desorption and adsorbent reuse.

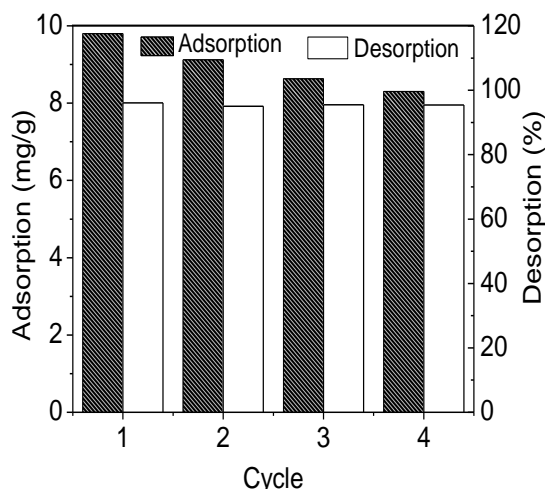


Fig. 7. Performance of ISMC by four adsorption-desorption cycles of regeneration

It was found that the chromium(VI) ions could be effectively desorbed from ISMC using 1.0 mol/L NaOH solution, with a desorption efficiency of over 95%. The capacity of adsorption reduced slightly in each cycle, and in the last cycle, the reduction was 16%. Therefore, ISMC can be easily regenerated and reused.

CONCLUSIONS

1. Fe(III)-loaded cotton linter (ISMC) was successfully synthesized by a reaction with succinylated mercerized cellulose and Fe(III), which had a 72 mg/g of Fe(III). ISMC rapidly removed chromium(VI) from an aqueous solution.
2. The optimum pH value for chromium(VI) adsorption by ISMC was 2, and its maximum chromium(VI) absorption capacity was 11.1 mg/g. The Langmuir model suitably depicted the adsorption equilibrium data. Adsorption followed a pseudo-second-order kinetic model. After four adsorption-desorption cycles, the reduction of adsorption capacity was 16%, which demonstrated that ISMC can be easily regenerated and reused.

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REFERENCES CITED

- Abdel-Halim, E. S., Abou-Okeil, A., and Hashem, A. (2006). "Adsorption of Cr(VI) oxyanions onto modified wood pulp," *Polym. Plast. Technol. Eng.* 45, 71-76. DOI: 10.1080/03602550500373519
- Albadarin, A. B., Mangwandi, C., Walker, G. M., Allen, S. J., Ahmad, M. N. M., and Khraisheh, M. (2013). "Influence of solution chemistry on Cr(VI) reduction and complexation onto date-pits/tea-waste biomaterials," *J. Environ. Manage.* 114, 190-201. DOI: 10.1016/j.jenvman.2012.09.017
- Bai, R. B., and Deng, S. B. (2004). "Removal of trivalent and hexavalent chromium with aminated polyacrylonitrile fibers: Performance and mechanisms," *Water Res.* 38(9), 2424-2432. DOI: 10.1016/S0043-1354(04)00122-8
- Bhatnagar, A., Kumar, E., and Sillanpää, M. (2011). "Fluoride removal from water by adsorption? A review," *J. Chem. Eng.* 171(3), 811-840. DOI: 10.1016/j.ccej.2011.05.028

- Cai, H. M., Chen, G. J., Peng, C. Y., Zhang, Z. Z., Dong, Y. Y., Shang, G. Z., Zhu, X. H., Gao, H. J., and Wan, X. C. (2015). "Removal of fluoride from drinking water using tea waste loaded with Al/Fe oxides: A novel, safe and efficient biosorbent," *App. Surf. Sci.* 328, 34-44. DOI: 10.1016/j.apsusc.2014.11.164
- Gurgel, L. V. A., de Melo, J. C. P., de Lena, J. C., and Gil, L. F. (2009). "Adsorption of chromium (VI) ion from aqueous solution by succinylated mercerized cellulose functionalized with quaternary ammonium groups," *Bioresour. Technol.* 100(13), 3214-3220. DOI: 10.1016/j.biortech.2009.01.068
- Gurgel, L. V. A., Karnitz Junior, O., de Freitas Gil, R. P., and Gil, L. F. (2008). "Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by cellulose and mercerized cellulose chemically modified with succinic anhydride," *Bioresour. Technol.* 99(8), 3077-3083. DOI: 10.1016/j.carbpol.2009.02.016
- Haron, M. J., Wan Yunus, W. M. Z., Wasay, S. A., Uchiumi, A., and Tokunaga, S. (1995). "Sorption of fluoride ions from aqueous solutions by Yttrium-loaded poly (hydroxamic acid) resin," *International Journal of Environmental Studies.* 48(3), 245-255. DOI: 10.1080/00207239508710994
- Ji, G. J., Bao, W. W., Gao, G. M., An, B. C., Zou, H. F., and Gan, S. C. (2012). "Removal of Cu (II) from aqueous solution using a novel crosslinked alumina-chitosan hybrid adsorbent," *Chinese J. Chem. Eng.* 20(4), 641-648. DOI: 10.1016/S1004-9541(11)60229-2
- Karnitz Júnior, O., Gurgel, L. V. A., Perin de Melo, J. C., Botaro, V. R., Melo, T. M. S., Gil, R. P. F. Gil, R. P. F., and Frédéric, L. (2007). "Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse," *Bioresour. Technol.* 98(6), 1291-1297. DOI: 10.1016/j.biortech.2006.05.013
- Liu, C. F., Zhang, A. P., Li, W. Y., and Sun, R. C. (2011). "Chemical modification of cellulose with succinic anhydride in ionic liquid with or without catalysts," in: *Ionic Liquids: Applications and Perspectives*, A. Kokorin (ed.), InTech, Rijeka, Croatia, pp. 81-94.
- Lo, I. M. C., and Mak, M. S. H. (2011). "Influences of redox transformation, metal complexation and aggregation of fulvic acid and humic acid on Cr(VI) and As(V) removal by zero-valent iron," *Chemosphere.* 84, 234-240. DOI: 10.1016/j.Chemosphere. 2011.04.024
- Mallick, S., Dash, S. S., and Parida, K. M. (2006). "Adsorption of hexavalent chromium on manganese nodule leached residue obtained from NH₃-SO₂ leaching," *J. Colloid Interf. Sci.* 297(2), 419-425. DOI: 10.1016/j.jcis.2005.11.001
- Mohanty, K., Jha, M., Biswas, M. N., and Meikap, B. C. (2005). "Removal of chromium(VI) from dilute aqueous solutions by activated carbon developed from *Terminalia arjuna* nuts activated with zinc chloride," *J. Chem. Eng. Sci.* 60(11), 3049-3059. DOI: 10.1016/j.ces.2004.12.049
- Namasivayam, C., and Sureshkumar, M.V. (2008). "Removal of chromium(VI) from water and wastewater using surfactant modified coconut coir pith as a biosorbent," *J. Bioresour. Technol.* 99(7), 2218-2225. DOI: 10.1063/1.119084
- Park, J. M., Park, D., Yun, Y. S., and Jo, J. H. (2005). "Mechanism of hexavalent chromium removal by dead fungal biomass of *Aspergillus niger*," *Water Res.* 39(4), 533-540. DOI: 10.1016/j.watres.2004.11.002
- Park, J. M., Park, D., Lim, S. R., and Yun, Y. S. (2007). "Reliable evidences that the removal mechanism of hexavalent chromium by natural biomaterials is adsorption-

- coupled reduction,” *Chemosphere* 70(2), 298-305. DOI: 10.1016/j.chemosphere.2007.06.007
- Park, D., Yun, Y. S., Jo, J. H., and Park, J. M. (2006a). “Biosorption process for treatment of electroplating wastewater containing Cr(VI): Laboratory-scale feasibility test,” *Ind. Eng. Chem. Res.* 45(14), 5059-5065. DOI: 10.1021/ie060002d
- Park, D., Yun, Y. S., Lim, S. R., and Park, J. M. (2006b). “Kinetic analysis and mathematical modeling of Cr(VI) removal in a differential reactor packed with ecklonia biomass,” *J. Microbiol. Biotechnol.* 16(11), 1720-1727.
- Shen, C. S., Chen, H., Wu, S. S., Wen, Y. Z., Li, L., Jiang, Z., Li, M. C., and Liu, W. P. (2013). “Highly efficient detoxification of Cr(VI) by chitosan – Fe(III) complex: Process and mechanism studies,” *J. Hazard. Mater.* 244–245(2), 689-697. DOI: 10.1016/j.jhazmat.2012.10.061
- Wu, P. X., Wu, W. M., Li, S. Z., Xing, N., Zhu, N. W., Li, P., Wu, J. H., Yang, C., and Dang, Z. (2009). “Removal of Cd²⁺ from aqueous solution by adsorption using Fe-montmorillonite,” *J. Hazard. Mater.* 169(1–3), 824-830. DOI: 10.1016/j.jhazmar.2009.04.022
- Yuchi, A., Matsungaga, K., Niwa, T., Terao, H., and Wada, H. (1999). “Separation and preconcentration of fluoride at the ng mL⁻¹ level with a polymer complex zirconium (IV) followed by potentiometric determination in a flow system,” *Analytic Chimica Acta.* 388, 201-208.
- Zhang, L. Z., Ai, Z. H., Cheng, Y., and Qiu, J. R. (2008). “Efficient removal of Cr(VI) from aqueous solution with Fe₂-Fe₂O₃ core-shell nanowires,” *J. Environ. Sci. Technol.* 42(18), 6955-6960. DOI: 10.1021/es800962m
- Zhao, Y. P., Li, X. Y., Li, L., and Chen, F. H. (2008). “Fluoride removal by Fe(III)-loaded ligand exchange cotton cellulose adsorbent from drinking water,” *Carbohydr. Polym.* 72(1), 144-150. DOI: 10.1016/j.carbpol.2007.07.038
- Zhao, Y. P., Huang, M. S., Wu, W., and Jin, W. (2009). “Synthesis of the cotton cellulose based Fe(III)-loaded adsorbent for arsenic(V) removal from drinking water,” *Desalination* 249(3), 1006-1011. DOI: 10.1016/j.desal.2009.09.015
- Zimmermann, A. C., Mecabo, A., Fagundes, T., and Rodrigues, C. A. (2010). “Adsorption of Cr(VI) using Fe-crosslinked chitosan complex (Ch-Fe),” *J. Hazard. Mater.* 179(1–3), 192-196. DOI: 10.1016/j.jhazmat.2010.02.078
- Zubair, A., Bhatti, N. N., Hanif, M. A., and Shafqat, F. (2008). “Kinetic and equilibrium modeling for Cr(III) and Cr(VI) removal from aqueous solutions by Citrus reticulata waste biomass,” *J. Water Air Soil Pollut.* 191(1), 305-318. DOI: 10.1007/s11270-0089626-y

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