Adsorption of hexavalent chromium on modified corn stalk using different cross-linking agents

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Abstract. In this study, four different types of adsorbents modified from corn stalk were synthesized after the reaction with epichlorohydrin, N,N-dimethylformamide, triethylamine and different cross-linking agents. The surface functional groups and thermal stability of modified corn stalk (MCSs) were characterized using FTIR and TG analysis, respectively. The feasibility of using MCSs to remove Cr(VI) were evaluated. Adsorption isotherms were determined and modeled with Langmuir, Freundlich and Temkin equations. The experimental results showed that MCS modified using diethylenetriamine (DETA) had the best modification effect, and the adsorption capacity of Cr(VI) reached as high as 227.27 mg/g at 323 K. Thermodynamic study showed that the Cr(VI) adsorption onto MCSs was endothermic processes. As a result, MCS by using DETA as cross-linking agent has good potential for the removal of Cr(VI) from aqueous solutions.

1. Introduction

Growing attention is being paid to the contamination of water system by traces of various heavy metal ions. The presence of heavy metals in the environment is hazardous due to their bioaccumulation in living tissues throughout the food chain and persistence [1, 2]. Among the various toxic heavy metals, chromium is on the top list of priority pollutants due to its carcinogenic and mutagenic properties defined by the U.S. Environmental Protection Agency (EPA) [2]. Chromium is present in aqueous system mainly in two stable oxidation states, trivalent chromium [Cr (III)] and hexavalent chromium [Cr (VI)]. Cr (VI) species has been considered more toxic and hazardous than Cr (III) species due to its highly solubility and mobility in the aqueous phase. Though most metals exist in a cationic form in natural aquatic system, Cr (VI) combined with oxygen is anionic. When pH is lower than 5, the Cr (VI) species may be mainly in the form of dichromate ($Cr_2O_7^{2-}$) and hydrogen chromate ($HCrO_4^-$) [3].

Cr(VI) is generated from many industrial processes such as electroplating, chromite mining, corrosion control, metal finishing industries, leather processing, wood preservation, inorganic chemical production and pulp production, etc. [2-5]. The maximum level concentration of Cr (VI) in drinking water is limited 0.05 mg/L recommended by World Health Organization (WHO) [6]. Therefore, removal of the Cr (VI) ions from their effluents is deemed essential.

Various technologies have been developed for treating Cr (VI) containing industrial wastewater, including adsorption, bio sorption, complication, electro-chemical precipitation, filtration, membrane ultrafiltration, reverse osmosis, microbial reduction and ion exchange [1-9]. Amongst the viable methods, the most mainly used ones are reverse osmosis, ion exchange and precipitation [7, 10]. Ion exchange is believed to have the main advantages of the potential recovery of the metal value, higher selectivity, less sludge volume produced and the meeting of strict discharge specifications [7]. Further development of ion exchange, IEX, has been investigated, i.e., the research of ion exchangers prepared from agricultural by-products. Some agricultural by-products such as rice hull, lauan sawdust, persimmon tealeaf and pine bark, straw, sugarcane bagasse, corn stalk, peanut shells, persimmon tealeaf, and soybean hulls have been converted into anion exchangers [11-15].

Corn stalk (CS) is regarded as abundant, low-cost and biodegradable resource available for the preparation of anion exchangers. The idea of converting CS into ion exchangers is based on the predominant contents of cellulose, hemicellulose and lignin that have a large amount of reactive hydroxyl groups. Modification reactions such as crosslinking and functionalization are commonly applied to enhance adsorption capacity and adsorbent chemical stability of the components present in agricultural by-products [11].

In our previous study [14], the modified corn stalk (MCS) using by diethylenetriamine (DETA) as the cross-linking agent showed good adsorption ability for Cr (VI) ions. However, a comparative study is still needed to improve our knowledge about the adsorption performance of corn stalk modified by different cross-linking agents such as DETA, triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). Therefore, an attempt in this work is made to evaluate their feasibility as an adsorbent for removal of Cr (VI) from aqueous solution. The characteristic and the adsorption capacities for Cr (VI) onto MCSs were determined in this paper.

2. Materials and method

2.1. Preparation of the anion exchangers
CS was obtained from the suburb of Jinan, Shandong, China. The raw corn stalk (RCS) was washed with deionized water, dried at 90oC for 24 h and then sieved into particles with diameters from 100 to 250 μm. Two grams of CS were reacted with 10 ml of epichlorohydrin and 12 ml of N, N-dimethylformamide (DMF) in a 250 ml three-neck round bottom flask at 100oC for 1 h. Four millilitres of different modifying agents was added and the solution was reacted for 1 h, followed by adding 15 ml of 99% triethylamine (w/w) for graft reaction. Mixture was reacted for and the mixture was stirred for 180 min at 100oC. When there was no modifying agent added, the product was namely MCS-1. As 4 mL of diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA) was added, the product was namely MCS-2, MCS-3, MCS-4, respectively.

2.2. Characterization techniques
The thermo gravimetric analysis (TGA) was carried out with a Q600 SDT synchronization thermal analyzer from 38°C to 600°C in N2 atmosphere with a heating rate of 10°C/min.

Knowledge of functional groups is very important because they influence the surface characteristics of the adsorbents. The functional groups presenting in RCS and MCS were investigated by using the fourier transform infrared spectrometer technique (PerkinElmer "Spectrum BX" spectrometer). The spectrum was scanned from 400 to 4000 cm-1.

2.3. Cr (VI) removal study
The stock chromium (VI) solutions (1000 mg/L) were prepared by dissolving 2.826 g of potassium dichromate (K2Cr2O7) (AR grade) in 1000 mL of distilled water. The stock solution was finally diluted to obtain standard solutions. All required concentrations were prepared by appropriately diluting of the stock standard solution.

2.3.1 Batch equilibrium studies. Equilibrium study on removal Cr (VI) was conducted in a batch system with accurately known amount of 0.1 g of MCS samples equilibrated with 50 mL of Cr (VI) solution of different initial concentrations (varying from 50 to 350 mg/L).in a 100-mL stoppered conical flasks. The conical flasks were applied by placing in a thermo stated water shaker at a constant speed of 150 rpm with temperatures 298, 318 and 333 K, respectively. The pH of the solutions was not adjusted (natural 4.76). After attaining equilibrium, 10-mL of each sample was withdrawn and filtered through 0.45 μm nitrocellulose membrane. The residual concentration of Cr (VI) was analysed by using a colorimetric method; the pink complex formed between 1, 5-diphenycarbazide and Cr (VI) was measured at 540 nm using a UV-vis. spectrophotometer (UV754GD, Shanghai) [16, 17]. All experiments were conducted in triplicate and the averages of the results are presented in this study. The measured Cr(VI) concentration was used to calculate the adsorption capacity, qe (mg/g), using the following expression:

$$q_e = \frac{(C_o - C_e)V}{W} \qquad (1)$$

Where Co and Ce are the initial and equilibrium concentration (mg/L), respectively; V is the volume of the solution (L) and W is the mass of adsorbent used (g).

3. Results and discussion

3.1. Characterization of the anion exchangers
Fig.1 shows the thermal stability of RCS and MCS with different modifying agents determined by TGA. It was showed that there was several weight loss steps observed of the studied materials distributed in the 28-600oC interval. The weight loss below 200oC is attributed to the evaporation of unbounded and physics orbed water [18]. However, the weight loss between 200 and 600oC may be attributed to the DE hydroxylation along with material decomposition of anion exchangers and DE hydroxylation only for RCS [19]. From the thermo gravimetric curves, it was observed that the weight loss of MCSs were all higher than RCS (77.4%) except for MCS-2 (76.2%). It was indicated that MCS-2 had better modification advantage than other modifying agents used in this study.
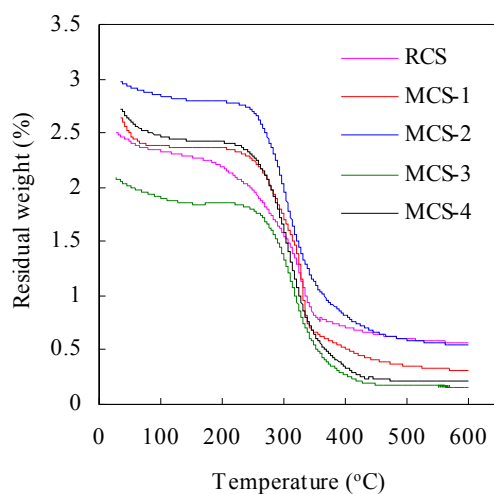
Fig.1 TGA results of raw corn stalk (RCS) and corn stalk (CS) with different modifying agents.

The pattern of sorption of metals onto materials is attributable to the active groups and bonds present on them [20]. In order to identify the main characteristic functional groups in the materials, FTIR analysis technique was used. Fig. 2 shows the FTIR spectrum of the MCSs and RCS. It displayed the characteristic cellulose bands in the finger print region of 1000-1200 cm-1, indicating that the main skeleton of fermented CS was the cellulose chains. The band appeared near at 1050 cm-1 of all samples except for MCS-1 corresponding to the C-O stretching vibration. A large vibration in the band at 1320 and 1374 cm-1 assigned to C-N stretching vibration suggests the grafted a large number of amine groups in the structure of the three cross-linking MCSs. The bands at observed near 2930 and 1650 cm-1 were attributed to the C-H bonds of aliphatic acids except for MCS-1 due to no cross-linking agent added. It was indicated that added cross-linking agent was good for amino groups grafted into the structure of the RWS. The broad bands observed at 3380-3410 cm were due to the stretching of O-H groups of macromolecular association in cellulose, hemicellulose, pectin, etc. for all the samples.
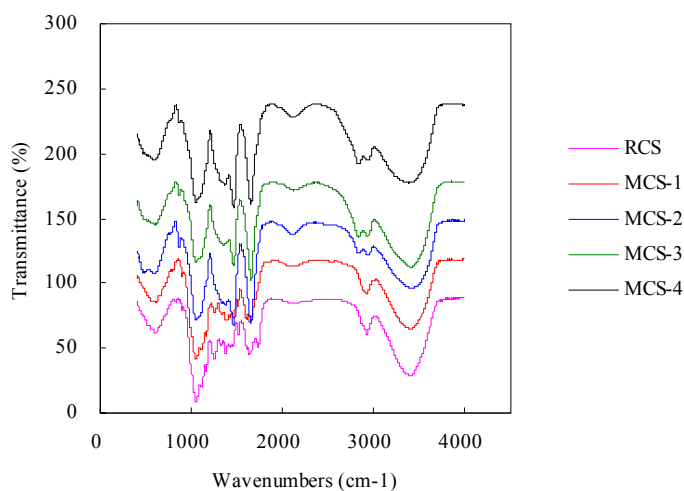

Fig.2 FTIR spectra of RCS and MCSs

3.2. Adsorption isotherms

Adsorption properties and equilibrium parameters, commonly known as adsorption isotherms, indicate the partition of adsorb ate between solution and adsorbent at equilibrium state. It is of immense importance in assessing the applicability of adsorption systems as a complete unit operation. In order to optimize the design of an operating procedure and to find the suitable model, it is essential to establish the most appropriate correlation for the equilibrium curves. The equilibrium adsorption data were interpreted using there isotherm models, namely, the Langmuir, Freundlich and Temkin.

The Langmuir isotherm model [21] is based on the assumption that sorption takes place at specific homogeneous sites onto the adsorbent surface with no lateral interaction between the adsorbed molecules, The Langmuir isotherm is valid for monolayer adsorption. It assumes the form:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (2)$$

Where qm is the monolayer adsorption capacity of the adsorbent (mg/g), KL is the Langmuir isotherm constant related to the adsorption energy (L/mg)

The linear form of the Langmuir isotherm can be represented by the following equation [22]:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \qquad (3)$$

By plotting 1/qe versus 1/Ce, qm and KL can be determined if a straight line is obtained.

The Freundlich isotherm model [23] is an exponential equation based on sorption process on heterogeneous surfaces or surface supporting sites of varied affinities. It assumes that a logarithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites [24] and is defined by:

$$q_e = K_F C_e^{1/n} \qquad (4)$$

Where KF and n are the Freundlich isotherm constants and 1/n is the adsorption intensity. The linear form of Freundlich isotherm is given as [4]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (5)$$

Temkin and Pyzhev [25] considered the effects of some indirect adsorb ate/adsorb ate interactions on adsorption isotherms and suggested that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to these interactions. The Temkin isotherm can be expressed in its linear form as:

$$q_e = B \ln A + B \ln Ce \qquad (6)$$

Where B and A are the Temkin constants and can be determined by a plot of qe versus lnCe.

The adsorption constants and model parameters calculated from the corresponding isotherms, along with the correlation coefficients (R2) are presented in Table 1. All values of R2 given in Table 1 were bigger than 0.9 except Tempkin model for MCS-2 (bigger than 0.87) and Freundlich model for MCS-4

at 298 K (bigger than 0.86). This phenomenon of latter is possibly attributed to its assumption of heterogeneous adsorbent surface, whereas the surface of MCS-4 is relatively uniform [26]. Thus, the three isotherms were all suitable equations to describe the adsorption equilibrium process, indicating the monolayer coverage of Cr (VI) ions onto the MCSs surface. The results for the adsorption capacity of Cr (VI) onto MCSs indicated that the modification of RCS by DETA has significantly enhanced the Cr (VI) uptake capacity compared with other modification. This indicated that the modification with DETA had more anionic adsorption sites than the other modification. As can be seen from Table 1, the adsorption capacity of the modification adsorbents was all increased with the temperature increased. On the other hand, the Langmuir constant KL also increased with the temperature showing the process to be endothermic [27]. The values of qm, KL and KF were all increased with increasing temperature, indicating that Cr (VI) can be easy removal by MCSs from aqueous solutions [22]. The values of 1/n obtained from the Freundlich model were below one, indicating a higher adsorption ability of Cr(VI) at all temperatures studied and also revealing the favorable adsorption of Cr(VI) onto MCSs [22,28]. Considering relatively larger Cr (VI) adsorption capacity of MCS-2, and DETA much lower price than TETA and TEPA, therefore, MCS-2 is a promising material for the removal of Cr (VI) from aqueous solutions.

Table 1Isotherm parameters for Cr (VI) sorption onto MCSs.

Adsorbent, T (K)	Langmuir			Freundlich			Tempkin		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)(L/mg)$^{1/n}$	$1/n$	R^2	A (L/mg)	B	R^2
MCS-1									
298	101.01	0.013	0.9422	5.041	0.512	0.9888	0.15	20.85	0.9410
308	105.26	0.016	0.9803	5.694	0.513	0.9929	0.17	22.24	0.9742
323	107.53	0.018	0.9669	6.821	0.489	0.9958	0.21	22.17	0.9609
MCS-2									
298	198.08	0.122	0.9742	79.26	0.192	0.9577	36.79	22.36	0.8963
308	206.36	0.163	0.9749	86.56	0.171	0.9646	69.29	20.78	0.8989
323	227.27	0.221	0.9771	99.72	0.17	0.9546	135.47	21.92	0.8750
MCS-3									
298	104.17	0.237	0.9948	48.053	0.165	0.9389	307.33	9.54	0.9862
308	117.65	0.298	0.9851	58.201	0.137	0.9914	4.04×10^3	8.12	0.9265
323	123.46	0.308	0.9879	61.301	0.144	0.9950	3.16×10^3	8.85	0.9412
MCS-4									
298	81.97	0.248	0.9349	58.183	0.218	0.8699	79.77	15.53	0.9743
308	142.86	0.684	0.9953	64.097	0.273	0.9037	97.73	16.56	0.9740
323	149.25	0.795	0.9931	74.582	0.179	0.9898	1.18×10^3	12.42	0.9194

3.3. Adsorption thermodynamics

Based on fundamental thermodynamic concept, it is assumed that in an isolated system, energy cannot be gained or lost and the entropy change is the only driving force [28]. To determine the effect of temperature on the adsorption process, the thermodynamic parameters such as change in the free energy change (ΔGo) enthalpy (ΔHo) and entropy (ΔSo) were calculated by using Eqs. (7) And (8) [28]:

$$\Delta G^o = -RT \ln K_L \qquad (7)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (8)$$

Where KL is the Langmuir isotherm constant, R is the gas constant (8.314 J/mol K) and T is the temperature (K). The ΔHo and ΔSo values calculated from the slope and intercept of the plots of ΔGo versus T are listed in Table 2.

Generally, the $\triangle G^o$ value for physical sorption is between -20 and 0 kJ/mol, and that for chemical sorption is between -400 and -80 kJ/mol. In this study, the values of $\triangle G^o$ were in the range of neither physical sorption nor chemical sorption, suggesting that the adsorption of Cr (VI) onto MCSs involves the other adsorption process such as ion exchange [18]. The values of $\triangle H^o$ were positive, indicating that the endothermic nature of adsorption reaction. The positive value of $\triangle S^o$ suggested the increasing randomness at the solid-liquid interface of Cr (VI) onto MCSs and the adsorption progress is spontaneous and favorable [22].

Table 2 Thermodynamic parameters for the adsorption of Cr (VI) on MCSs.

Parameters	T (K)	MCS-1	MCS-2	MCS-3	MCS-4
	298	10.76	5.21	3.57	3.45
$\triangle G^o$ (kJ/mol)	308	10.59	4.65	3.10	0.97
	323	10.79	4.05	3.16	0.62
$\triangle H^o$ (kJ/mol)		10.06	18.82	7.79	34.65
$\triangle S^o$ (J/mol K)		$-$ 0.002	0.046	0.015	0.107

4. Conclusion

In this study, corn stalk was used as precursor material for the preparation of adsorbents modified by DETA, TETA and TEPA, and their sorption performances were investigated for the removal of Cr (VI) from aqueous solutions. The FTIR spectrums analysis indicated that a large number of amino groups with positive charge were successfully grafted in the structure of MCSs. The adsorption isotherms study revealed that the equilibrium data were best described by the Langmuir isotherm models in all cases. The Cr (VI) adsorption capacity was enhanced by DETA modified corn stalk. The maximum adsorption capacity of MCS-2 obtained was 227.27 mg/g at 323 K. The positive values of $\triangle H^o$ showed the endothermic nature of adsorption reaction and the positive values of $\triangle S^o$ confirmed the affinity of Cr (VI) for MCSs. Thermodynamic studies demonstrated the adsorption process of Cr (VI) onto MCSs involved ion exchange. The present study showed that the CS modified by DETA had relatively larger Cr (VI) adsorption capacity than by no cross-ling agent, TETA and TEPA, therefore, MCS-2 is a promising material for the removal of Cr (VI) from aqueous solutions.

References

[1] H.D. Choi, W.S. Jung, J.M. Cho, B.G. Ryu, J.S. Yang, K. Baek, Adsorption of Cr(VI) onto cationic surfactant-modified activated carbon, J. Hazard. Mater. 166 (2009) 642-646.

[2] G. Bayramoğlu, M.Y. Arica, Adsorption of Cr (VI) onto PEI immobilized acrylate-based magnetic beads: Isotherms, kinetics and thermodynamcis study, Chem. Eng. J. 139 (2008) 20-28.

[3] E.M. Contreras, A.M. Ferro Orozco, N.E. Zaritzky, Biological Cr(VI) removal coupled with biomass growth, biomass decay, and multiple substrate limitation. Water Res. 45 (2011) 3034-3046.

[4] S.S. Baral, S.N. Das, G. Roy Chaudhury, Y.V. Swamy, P. Rath, Adsorption of Cr(VI) using thermally activated weed Salvinia cucullata. Chem. Eng. J. 139 (2008) 245-255.

[5]   P.E. Molokwane, K.C. Meli, and E.M. Nkhalambayausi-Chirwa, Chromium (VI) reduction in activated sludge bacteria exposed to high chromium loading: Brits culture (South Africa). Water Res. 42 (2008) 4538-4548.

[6]   L. Cheng, X.C. Li, R.X. Jiang, C. Wang, H.B. Yin, Effects of Cr(VI) on the performance and kinetics of the activated sludge process. Bioresour. Technol. 102 (2011) 797-804.

[7]   B. Galán, D. Castañeda, I. Ortiz, Removal and recovery of Cr (VI) from polluted ground waters: A comparative study of ion-exchange technologies. Water Res. 39 (2005) 4317-4324.

[8]   G.L. Huang, J.X. Shi, T.A.G. Langrish, Removal of Cr (VI) from aqueous solution using activated carbon modified with nitric acid. Chem. Eng. J. 152 (2009) 434-439.

[9]   L.N. Shi, X. Zhang, Z.L. Chen, Removal of Chromium (VI) from wastewater using bentonite-supported nanoscale zero-valent iron. Water Res. 45 (2011) 886-892.

[10] R.S. Bai, T.E. Abraham, Studies on enhancement of Cr (VI) biosorption by chemically modified biomass of Rhizopus nigricans. Water Res. 36 (2002) 1224-1236.

[11] U.S. Orlando, A.U. Baes, W. Nishijima, M. Okada, Preparation of agricultural residue anion exchangers and its nitrate maximum adsorption capacity. Chemosphere 48 (2002) 1041-1046.

[12] T.E. Köse, Agricultural residue anion exchanger for removal of dyestuff from wastewater using full factorial design. Desalination 222 (2008) 323-330.

[13] U.S. Orlando, A.U. Baes, W. Nishijima, M. Okada, A new procedure to produce lignocellulosic anion exchangers from agricultural waste materials. Bioresour. Technol. 83 (2002) 195-198.

[14] S.H. Chen, Q.Y. Yue, B.Y. Gao, Q. Li, X. Xu, Removal of Cr(VI) from aqueous solution using modified corn stalks: Characteristic, equilibrium, kinetic and thermodynamic study. Chem. Eng. J. 168 (2011) 909-917.

[15] L.H. Wartelle, W.E. Marshall, Quaternized agricultural by-products as anion exchange resins. J. Environ. Manage. 78 (2006) 157-162.

[16] Y.A. Aydın, N.D. Aksoy, Adsorption of chromium on chitosan: Optimization, kinetics and thermodynamics. Chem. Eng. J. 151 (2009) 188-194.

[17] S.B. Deng, Y.P. Ting, Polyethylenimine-Modified Fungal Biomass as a High-Capacity Biosorbent for Cr (VI) Anions: Sorption Capacity and Uptake Mechanisms. Environ. Sci. Technol. 39 (2005) 8490-8496.

[18] J.W. Lin, Y.H. Zhan, Z.L. Zhu, Y.Q. Xing, Adsorption of tannic acid from aqueous solution onto surfactant-modified zeolite. J. Hazard. Mater. 193 (2011) 102-111.

[19] A.M. Donia, A.A. Atia, W.A. Al-amrani, A.M. El-Nahas, Effect of structural properties of acid dyes on their adsorption behaviour from aqueous solutions by amine modified silica. J. Hazard. Mater. 161 (2009) 1544-1550.

[20] M. Iqbal, A. Saeed, S.I. Zafar, FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd2+ and Pb2+ removal by mango peel waste. J. Hazard. Mater. 164 (2009) 161-171

[21] I. Langmuir, The constitution and fundamental properties of solids and liquids. Part I solids, J. Am. Chem. Soc. 38 (1916) 2221-2295.

[22] R.P. Han, J.J. Zhang, P. Han, Y.F. Wang, Z.H. Zhao, M.S. Tang, Study of equilibrium, kinetic and thermodynamic parameters about methylene blue adsorption onto natural zeolite. Chem. Eng. J. 145 (2009) 496-504

[23] H.M.F. Freundlich, Uber die adsorption in lasungen, Z. Phys. Chem. 57 (1906) 385-70.

[24] C.C.V. Cruz, A.C.A. da Costa, C.A. Henriques, A.S. Luna, Kinetic modeling and equilibrium studies during cadmium biosorption by dead Sargassum sp. Biomass. Bioresour. Technol. 91 (2004) 249-257.

[25] M.I. Temkin, V. Pyzhev, Kinetics of ammonia synthesis on promoted iron catalyst, Acta Physiochim. URSS 12 (1940) 327-356.

[26] Q.S. Liu, T. Zheng, P. Wang, J.P. Jiang, N. Li, Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers. Chem. Eng. J. 157 (2010) 348-356.

[27] T. Zhang, Q.R. Li, Y. Liu, Y.L. Duan, W.Y. Zhang, Equilibrium and kinetics studies of fluoride ions adsorption on CeO2 /Al2O3 composites pretreated with non-thermal plasma. Chem. Eng. J. 168 (2011) 665-671.

[28] R.I., B. El-Eswed, A.H. Al-Muhtaseb, Adsorption characteristics of natural zeolites as solid adsorbents for phenol removal from aqueous solutions: Kinetics, mechanism, and thermodynamics studies. Chem. Eng. J. 171 (2011) 1143-1149.