Original Research Paper

Open Access

Optimized Preparation and Cr(VI) Adsorption Property Study of Activated Blue-coke

Yuhong Tian*†, Shudi Hu*, Xiaowei Chi, Xinzhe Lan*†, Yonghui Song* and Le Ju***

*School of Metallurgical Engineering, Xi'an University of Architecture and Technology, Xi'an, 710055, China
Research Centre on Metallurgical Engineering and Technology of Shaanxi Province, Shaanxi Key Laboratory of Gold and Resource, Xi'an, 710055, China
**Department of Chemistry, Oakland University, Michigan, 48309, United States
***Xi'an Gaoxin No.1 High School, Xi'an, 710065, China
†Corresponding authors: Yuhong Tian, Xinzhe Lan

ABSTRACT

The present work explored the use of solid waste fine blue-coke as a feedstock for the preparation of activated blue-coke and its adsorption property of Cr(VI). Chemical activation of this precursor, using KOH as activating agent, was adopted. The properties of activated blue-coke were characterized by N_2 adsorption isotherms. The results show that the iodine number is 1202 mg/g, the Brunauer-Emmett-Teller (BET) surface area is 1368.18 m²/g and the total pore volume is 0.6745 cm³/g, when the activated blue-coke prepared at the optimized conditions: KOH/fine blue-coke ratio at 4, 800°C activated temperature, 60 min activated time. The adsorption properties of activated coke on Cr(VI) were discussed. The regression results show that the adsorption kinetics is more accurately expressed as a pseudo second order model. The linear correlation coefficients of the Langmuir and Freundlich isotherms were determined and the results reveal that the Freundlich isotherm fits the experimental results better.

INTRODUCTION

The wastewater produced by mining industries, metal cleaning, the dyes, electroplating and leather contains a considerable amount of chromium (VI) ions (Acharya et al. 2009). Chromium (VI) ions are toxic to the human body. The environmental pollution caused by Cr(VI) ions has been paid more and more attention (Deflora et al. 1990, Leonard & Lauwerys 1980). The main techniques for removing Cr(VI) from wastewater include chemical precipitation, membrane, ion exchange, adsorption, filtration electro-deposition, biological processes, etc. (Liu et al. 2010). Among these techniques, adsorption has been proven to be a reliable and effective method for the treatment of toxic heavy metal wastewater (Karthik & Meenakshi 2015, Kumar et al. 2015, Liu et al. 2014).

Activated carbon is a kind of adsorbent with highly developed porosity and high degree of surface reactivity, which is widely used in multiple areas (Li et al. 2009). However, its application is limited due to the high cost and difficult regeneration of activated carbon (Fu et al. 2011, Hernandez-Ramirez & Holmes 2008, Ozdemir & Yapar 2009). Over the last few years, many researchers have explored the use of cheap and high quality adsorbents instead of commercial activated carbon, such as semi-coke (Gao et al. 2015, Wang et al. 2013, Wei et al. 2016), agricultural residues (Mahmood-ul-Hassan et al. 2015, Miretzky & Cirelli 2010), plant wastes (Gupta et al. 2013, Saranya & Thirumarimurugan 2015) and some other solid wastes (Deng et al. 2016, Kumar & Jena 2017, Song et al. 2016). It not only decreases the cost of adsorbent, but also is of great environment protection value.

Blue coke is a product after carbonization of long flame coal at low temperature (Lan et al. 2009). Fine blue-coke is a low value product in the production process of blue coke, the particle size less than 3 mm counts about 10% (Xiaojun 2007), which cannot be used in conventional reduction process because of its small particle size. And most can be treated as low-grade fuel or discarded. Recently, with the rapid development of low-temperature carbonization of coal industry, there is serious backlog of fine blue-coke, which not only takes up a lot of land, but also pollutes the soil environment (Tian et al. 2015). The physical and chemical properties of fine blue-coke are high fixed carbon content, low ash and volatile content of high strength. So it is a promising raw material for production of adsorbent (Yongjun et al. 1998, Zhang et al. 1999). However, due to the presence of tar and ash on its surface, the blue-coke has a low adsorp-

tion capacity (Inoue & Kawamoto 2005). The adsorption capacity of blue-coke is lower than activated carbon. So in order to improve the adsorption performance, we need to modify the blue-coke.

This paper focuses on preparation of activated blue-coke by chemical activation method with KOH activating agent and evaluation of its Cr(VI) adsorption characteristics. The preparation conditions of activated blue-coke were optimized by systematically studying the KOH/fine blue-coke ratio, activation temperature and activation time. Also, the surface structure properties of activated blue-coke were investigated. In order to estimate the removal efficiency of activated blue-coke, some kinetic and isotherm models were used to fit the experimental data.

MATERIALS AND METHODS

Materials: Fine blue-coke is by-product of Shenmu Sanjiang Coal Chemical Liability Co., Ltd. located in Yulin city. Its moisture content is 2.88 wt%, volatile content is 3.95 wt% and ashes content is about 9.44 wt%. The fine blue-coke particle size range of 1 mm-2.36 mm was used for the preparation of activated blue-coke.

Preparation methods: Fine blue-coke was mixed with KOH intensively according to the mass ratio of KOH to fine blue-coke. The mixture was placed in stainless steel boat and then placed in activating oven. They were heated to a certain temperature under nitrogen protection by programmed temperature controlling. The process of activation temperature elevation was as follows: constant-temperature heating at 110°C for 30 min in order to get rid of the moisture in the mixing process; constant-temperature heating at 400°C for 20 min in order to achieve full contact of KOH fusion with fine blue-coke, since fusing point of KOH is 360°C. The heating rate kept 10°C/min in the whole process of temperature elevation. Activation products were cooled under nitrogen to room temperature. These samples were soaked in 5% HCl for 12 h and washed with distilled water until washing solution pH reached 7, then dried at 110°C for 8 h.

Orthogonal experiment: For a comprehensive investigation of alkali dosage, activation temperature and activation time influence on adsorption property of activated blue-coke, and use as few experimental times as possible to obtain optimum conditions, $L_9(3^4)$ matrix orthogonal design was used in this experiment. The factors and levels of orthogonal experiment are listed in Table 1.

Analysis method: The iodine number (mg of iodine adsorbed/g of carbon) of activated blue-coke was determined according to GB/T 7702.7-2008. Specific surface area and pore structure analysis of activated blue-coke were deter-

Table 1: Factors and levels of the orthogonal experiment.

Level	Ratio ($m_{OH}:m_C$)	Activated temperature(°C)	Activated time(min)
1	2	750	60
2	3	800	90
3	4	850	120

m_{OH}: amount of potassium hydroxide; m_C: amount of fine blue-coke

mined by measuring nitrogen adsorption-desorption isotherms in an automatic adsorption instrument (Micromeritics, ASAP 2020). Adsorption of N_2 was performed at liquid nitrogen temperature (77 K). Prior to the measurements, the samples were degassed by purging with N_2 flow at 350°C for 2 h. Specific surface area was estimated by BET method using N_2 adsorption isotherm data. Pore distribution was derived from BJH theory and pore volume was deduced from adsorption data.

Cr(VI) adsorption: Adsorption kinetic experiments were conducted as follows: 0.25 g activated blue-coke was added to each Cr(VI) solution (50 mL) with an initial concentration of 50 mg/L. Afterwards, mixture was filtrated after shaking the mixture at 298 K, 308 K, 318 K respectively, for different times ranging from 20 min to 120 min, and then Cr(VI) concentration of the filtrate solution was measured.

Determination of Cr(VI) equilibrium adsorption from an aqueous solution was carried out as follows: 0.25 g activated blue-coke was added to each Cr(VI) solution (50 mL) with an initial concentration from 10 mg/L to 200 mg/L. Then, the mixture was filtrated after shaking it at 298 K, 308 K and 318 K respectively for 120 min, and then Cr(VI) concentration of the filtrate solution was measured. Cr(VI) concentration in the solution was determined by diphenyl carbazide spectrophotometric method at 540 nm wavelength.

RESULTS AND DISCUSSION

Optimization of preparation conditions: The results of design and range analysis of the orthogonal experiment are given in Table 2.

As presented in Table 2, the order of factors affecting iodine number is A>B>C with a decrease sequence of R. The results of K are $K_3(A)>K_2(A)>K_1(A)$, $K_2(B)>K_3(B)>K_1(B)$ and $K_1(C)>K_3(C)>K_2(C)$. Therefore, the best combination is $A_3B_2C_1$, that is, the optimized conditions for preparation of activated blue-coke are as follows: the KOH/coke ratio 4, activation temperature 800°C and activation time 60 min.

The orthogonal experiment results were analysed by orthogonal design assistant software IIV3.1. The variance analysis results are depicted in Table 3. F_A and F_B are larger

Table 2: Design and visual analysis of the orthogonal experiment.

Number	Ratio(m_{OH}:m_C)	Activated temperature(°C)	Activated time(min)	Blank	Iodine number (mg/g)
1	1	1	1	1	848
2	1	2	2	2	959
3	1	3	3	3	926
4	2	1	2	3	917
5	2	2	3	1	1086
6	2	3	1	2	1016
7	3	1	3	2	996
8	3	2	1	3	1202
9	3	3	2	1	1086
K_1	911.000	920.333	1022.000	1006.667	
K_2	1006.333	1082.333	987.333	990.333	
K_3	1094.667	1009.333	1002.667	1015.000	
R	183.667	162.000	34.667	24.667	

Blank: experimental error. m_{OH}: amount of potassium hydroxide. m_C: amount of fine blue-coke. K (K_1, K_2, K_3) is the average of Iodine number for each factor at different levels. R= $k_{i(max)}$-$k_{i(min)}$

Table 3: Analysis results of variance.

Resource of variance	Sum of square of deviations	Degree of freedom	F Value	Significance
A	50624.667	2	53.590	*
B	39494.000	2	41.807	*
C	1810.667	2	1.917	
Blank(Error)	944.67	2	F0.05 (2,2)=19	

Table 4: First-order and second-order adsorption rate constants of Cr(VI) onto activated blue-coke.

T		Pseudo-first-order				Pseudo-second-order		
	q_e/(mg g^{-1})	k_1	q_e.c	R^2	k_2	q_e.c	R^2
298	9.24	0.049	5.85	0.9776	0.016	9.77	0.9995
308	8.90	0.047	5.73	0.9877	0.015	9.47	0.9985
318	8.20	0.044	5.65	0.9787	0.013	8.83	0.9992

than F critical value, which indicates that the KOH/coke ratio and activation temperature have larger effects on activated blue-coke iodine number. F_C is much less than F, which indicates that activated time, has smaller effect on activated blue-coke iodine number. The variance analysis results coincide with range analysis results.

Characterization of activated blue-coke: N$_2$ adsorption is considered to be a standard method for the characterization of carbonaceous adsorbents porosity texture. The isotherm can provide information about the porous structure of adsorbent, adsorption heat, physical and chemical properties, and so on (Önal 2006, Shi et al. 2010).

The N$_2$ adsorption-desorption isotherm and pore size distribution of activated blue-coke prepared under optimized conditions are shown in Fig. 1 and Fig. 2.

As shown in Fig. 1, the isotherm is more of type II character according to the International Union of Pure and Applied Chemistry (IUPAC) classification. When P/P$_0$ is more than 0.2, the adsorption capacity increases as the relative pressure continues to increase, but the upward trend is slow, resulting in adsorption platform which is not horizontal, has a certain slope and appears tailing at high pressure (Marsh & Reinoso 2006). The adsorption quantity rises along with the increase of relative pressure because of the occurrence of multilayer adsorption and capillary condensation at high pressure. These indicate that activated blue-coke made from fine blue-coke is predominantly microporous, but also with a small amount mesopores and macropores. The activated blue-coke has a high surface area of 1368.18 m^2/g, that is primarily attributed to the microporous and mesoporous structure. The total pore
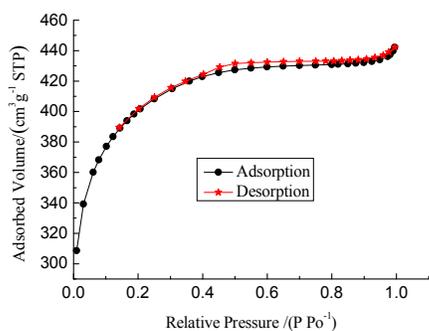
Fig. 1: Adsorption-desorption isotherms of activated blue-coke.
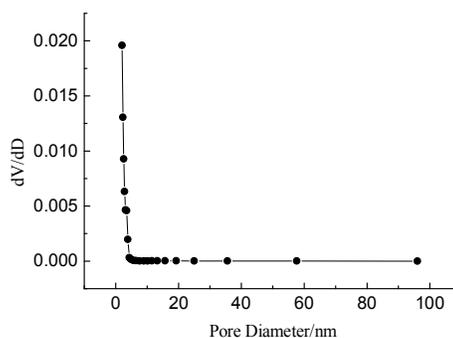
Fig. 2: Pore size distribution of activated blue-coke.
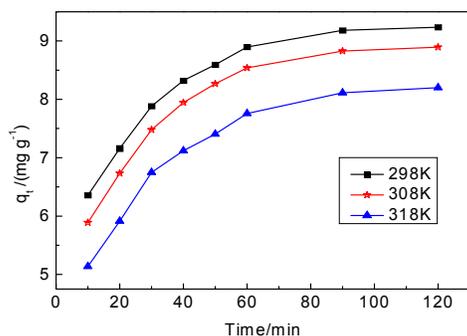
Fig. 3: Adsorption kinetic curve of activated blue-coke on
Cr(VI) at different temperature.
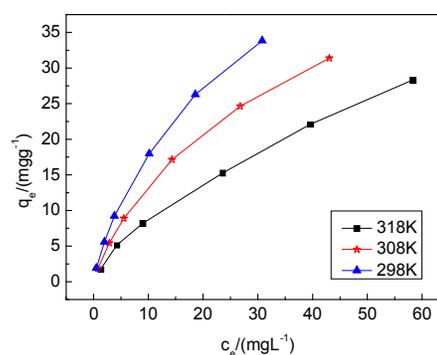
Fig. 4: Asorption isotherms of Cr(VI) at different temperatures.
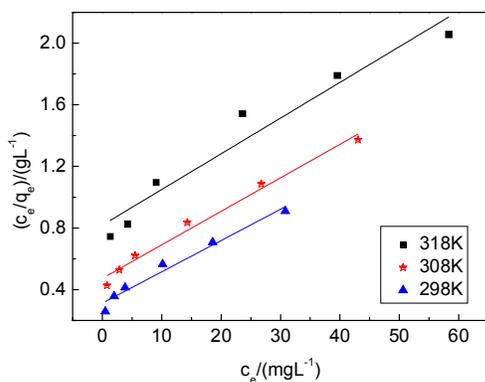
Fig. 5: Langmuir isotherms for the adsorption of Cr(VI)
at different temperatures.
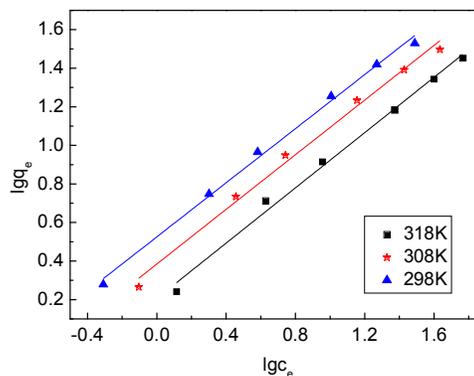
Fig. 6: Freundlich isotherms for the adsorption Cr(VI)
at different temperatures

volume is as high as 0.6745 cm³/g. As shown in Fig. 2, a mesopore size distribution is obtained with a peak at about 3 nm. The average mesopore size is equal to 2.7335 nm.

Kinetics of adsorption: In order to investigate the adsorption rate of activated blue-coke for Cr(VI), the effect of contact time between adsorbent and Cr(VI) on adsorptive capacity was investigated in conditions of initial concentrations of Cr(VI) 50 mg/L, pH of 4 and dosage of activated

blue-coke 0.1 mg/L.

The influence of time on Cr(VI) adsorption at different temperatures is shown in Fig. 3. Obviously, the time has a significant impact on the adsorption within 60 min. However, adsorption becomes slow after 60 min. The amount of adsorption is no longer increased after 120 min as the adsorption is balanced.

Analysis of adsorption kinetics is done using Lagergren's

pseudo-first-order (1) and pseudo-second-order rate equations (2) (Almeida et al. 2009, Lagergren 1898, Palanisamy & Sivakumar 2009).

$$lg(q_e - q_t) = lg\, q_e - \frac{k_1 t}{2.303} \qquad ...(1)$$

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

Where, q_t and q_e are the amount of Cr(VI) adsorption at time t, and at equilibrium, mg g^{-1}. k_1 is the equilibrium rate constant of first-order adsorption, min^{-1}. k_2 is the equilibrium rate constant of second-order adsorption, g mg^{-1} min^{-1}. The values of q_e and k_1 can be calculated from the intercept and slope of the plot $l_g(q_e-q_t)$ versus t. The values of $1/k_2 q_{e2}$ and $1/q_e$ can be determined from the intercept and slope of the plot t/q_t versus t.

Fitting the experimental data utilizing mathematic models, the data are presented in Table 4. The results show that the linear regression coefficient of the pseudo-second-order is > 0.99, and apparently is larger to the linear correlation coefficient of the pseudo-first-order . The calculated values of q_e are very close to the experimental values in pseudo-second-order. The experimental data show that the adsorption process kinetics is fitted well using the pseudo-second-order reaction model.

Adsorption isotherms: The Langmuir adsorption isotherm can be expressed as (Langmuir 1918, Mellah et al. 2006):

$$q_e = q_{max} \frac{bC_e}{1 + bC_e} \qquad ...(3)$$

Linear form of the rearranged Langmuir model is:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b \cdot q_{max}} \qquad ...(4)$$

Fig. 4 shows the adsorption isotherms of activated blue-coke on Cr(VI) adsorption at different temperatures. The experimental data are linear fitted by Langmuir isothermal equation and Freundlich isothermal equation. The results of Fig. 5 and Fig. 6 and the correlation parameter are presented in Table 5.

The Freundlich adsorption isotherm can be expressed as (Freundlich 1906, Mellah et al. 2006):

$$q_e = KC_e^{1/n} \qquad ...(5)$$

Linear form of Freundlich equation is:

$$lg\, q_e = lg\, K + \frac{1}{n} lg\, C_e \qquad ...(6)$$

Langmuir and Freundlich isotherms are suitable models to analyse the equilibrium data for the Cr(VI) adsorption, however, the Freundlich model fits better than the Langmuir model. The values of K and 1/n in Freundlich equation can be calculated from the intercept and slope of the plot $lg\, q_e$ versus $lg\, C_e$. The value of K indicates the relative magnitude of adsorption capacity. The constant of n is relative to the strength of adsorption impetus. The value of K decreased and n increased with the rise of temperature, this shows that adsorption of Cr(VI) is exothermic.

CONCLUSIONS

Activated blue-coke was successfully prepared from fine blue-coke by chemical activation with KOH. Orthogonal analysis was used to investigate the factors influencing the iodine number and obtained the optimized conditions. At the optimized conditions, the BET surface area, total pore volume and average pore size of activated blue-coke are 1368.18 m^2/g, 0.6745 cm^3/g and 1.9720 nm, respectively. The adsorption system follows pseudo-second-order kinetics. Freundlich isotherm model fits the experimental data better compared with Langmuir isotherm model. Thus, activated blue-coke made from discarded fine blue-coke is a promising material for adsorption of Cr(VI).

ACKNOWLEDGMENTS

REFERENCES

Acharya, J., Sahu, J.N., Sahoo, B.K., Mohanty, C.R. and Meikap, B. C. 2009. Removal of chromium (VI) from wastewater by activated carbon developed from tamarind wood activated with zinc chloride. Chemical Engineering Journal, 150(1): 25-39.

Table 5: Langmuir and Freundlich parameters for adsorption of Cr(VI) onto activated blue-coke at different tempertures.

Temperature (K)	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
	q_{max}	B	R^2	n	K	R^2
298	49.24	0.0650	0.9665	1.426	3.3523	0.9952
308	45.98	0.0460	0.9812	1.412	2.4252	0.9915
318	43.16	0.0283	0.9380	1.396	1.6088	0.9924

Almeida, C., Debacher, N., Downs, A., Cottet, L. and Mello, C. 2009. Removal of methylene blue from colored effluents by adsorption on montmorillonite clay. Journal of Colloid and Interface Science, 332(1): 46-53.

Deflora, S., Bagnasco, M., Serra, D. and Zanacchi, P. 1990. Genotoxicity of chromium compounds - a review. Mutation Research, 238(2): 99-172.

Deng, Y., Morris, C., Rakshit, S., Landa, E., Punamiya, P. and Sarkar, D. 2016. Water treatment residuals and scrap tire rubber as green sorbents for removal of stormwater metals. Water Environment Research, 88(6): 500-509.

Freundlich, H. 1906. Uber die adsorption in lasugen. J. Phys. Chem., 57: 385-470.

Fu, F., Gao, Z., Gao, L. and Li, D. 2011. Effective adsorption of anionic dye, alizarin red S, from aqueous solutions on activated clay modified by iron oxide. Industrial & Engineering Chemistry Research, 50(16): 9712-9717.

Gao, X., Zhai, X., Wang, Z., Fu, F. and Li, W. 2015. Effective adsorption of phenol from aqueous solutions on activated semi-coke. Journal of Materials Science, 50(12): 4200-4208.

Gupta, V.K., Pathania, D., Agarwal, S. and Sharma, S. 2013. Removal of Cr(VI) onto *Ficus carica* biosorbent from water. Environmental Science and Pollution Research, 20(4): 2632-2644.

Hernandez-Ramirez, O. and Holmes, S.M. 2008. Novel and modified materials for wastewater treatment applications. Journal of Materials Chemistry, 18(24): 2751-2761.

Inoue, K. and Kawamoto, K. 2005. Fundamental adsorption characteristics of carbonaceous adsorbents for 1, 2, 3, 4-tetrachlorobenzene in a model gas of an incineration plant. Environmental Science & Technology, 39(15): 5844-5850.

Karthik, R. and Meenakshi, S. 2015. Removal of Cr(VI) ions by adsorption onto sodium alginate-polyaniline nanofibers. International Journal of Biological Macromolecules, 72: 711-717.

Kumar, A. and Jena, H. M. 2017. Adsorption of Cr(VI) from aqueous solution by prepared high surface area activated carbon from fox nutshell by chemical activation with H_3PO_4. Journal of Environmental Chemical Engineering, 5(2): 2032-2041.

Kumar, A.S.K., Jiang, S.J. and Tseng, W.L. 2015. Effective adsorption of chromium(VI)/Cr(III) from aqueous solution using ionic liquid functionalized multiwalled carbon nanotubes as a super sorbent. Journal of Materials Chemistry A, 3(13): 7044-7057.

Lagergren, S. 1898. About the theory of so-called adsorption of soluble substances. Kungliga Svenska Vetenskapsakademiens Handlingar, 24(4): 1-39.

Lan, X., Yang, Y., Song, Y., Zhang, Q., Shang, W. and Luo, W. 2009. Energy consumption analysis of carbonization process of semi-coke in northern Shaanxi. Coal Conversion, 32(2): 18-21.

Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. Journal of the American Chemical Society, 40(9): 1361-1403.

Leonard, A. and Lauwerys, R.R. 1980. Carcinogenicity and mutagenicity of chromium. Mutation Research, 76(3): 227-239.

Li, W., Peng, J.H., Zhang, L., Yang, K.B., Xia, H.Y., Zhang, S.M. and Guo, S.H. 2009. Preparation of activated carbon from coconut shell chars in pilot-scale microwave heating equipment at 60 kW. Waste Management, 29(2): 756-760.

Liu, H., Liang, S., Gao, J.H., Ngo, H.H., Guo, W.S., Guo, Z.Z., Wang, J. and Li, Y.R. 2014. Enhancement of Cr(VI) removal by modifying activated carbon developed from *Zizania caduciflora* with

tartaric acid during phosphoric acid activation. Chemical Engineering Journal, 246: 168-174.

Liu, W.F., Zhang, J.A., Zhang, C.L., Wang, Y.F. and Li, Y. 2010. Adsorptive removal of Cr(VI) by Fe-modified activated carbon prepared from *Trapa natans* husk. Chemical Engineering Journal, 162(2): 677-684.

Mahmood-ul-Hassan, M., Suthar, V., Rafique, E., Ahmad, R. and Yasin, M. 2015. Kinetics of cadmium, chromium, and lead sorption onto chemically modified sugarcane bagasse and wheat straw. Environmental Monitoring and Assessment, 187(7).

Marsh, H. and Reinoso, F.R. 2006. Activated Carbon, Elsevier.

Mellah, A., Chegrouche, S. and Barkat, M. 2006. The removal of uranium(VI) from aqueous solutions onto activated carbon: kinetic and thermodynamic investigations. Journal of Colloid and Interface Science, 296(2): 434-441.

Miretzky, P. and Cirelli, A.F. 2010. Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: a review. Journal of Hazardous Materials, 180(1-3): 1-19.

Önal, Y. 2006. Kinetics of adsorption of dyes from aqueous solution using activated carbon prepared from waste apricot. Journal of Hazardous Materials, 137(3): 1719-1728.

Ozdemir, G. and Yapar, S. 2009. Adsorption and desorption behavior of copper ions on Na-montmorillonite: effect of rhamnolipids and pH. Journal of Hazardous Materials, 166(2-3): 1307-1313.

Palanisamy, P. and Sivakumar, P. 2009. Kinetic and isotherm studies of the adsorption of acid blue 92 using a low-cost non-conventional activated carbon. Desalination, 249(1): 388-397.

Saranya, K. and Thirumarimurugan, M. 2015. Comparative studies on removal of chromium(VI) from monocotyledon (*Allium cepa*) tunic and dicotyledon plant (*Tabebuia aurea*). Polish Journal of Environmental Studies, 24(3): 1291-1297.

Shi, Q. Q., Zhang, J., Zhang, C. L., Li, C., Zhang, B., Hu, W. W., Xu, J. T. and Zhao, R. 2010. Preparation of activated carbon from cattail and its application for dyes removal. Journal of Environmental Sciences, 22(1): 91-97.

Song, M., Wei, Y.X., Yu, L. and Tang, X.H. 2016. The application of prepared porous carbon materials: effect of different components on the heavy metal adsorption. Waste Management & Research, 34(6): 534-541.

Tian, Y.H., Lan, X.Z., Song, Y.H., Liu, C.B. and Zhou, J. 2015. Preparation and characterization of formed activated carbon from fine blue-coke. International Journal of Energy Research, 39(13): 1800-1806.

Wang, X., Peng, J.H., Duan, X.H. and Srinivasakannan, C. 2013. Preparation of modified semi-coke by microwave heating and adsorption kinetics of methylene blue. Journal of Microwave Power and Electromagnetic Energy, 47(2): 110-125.

Wei, F. Y., Wu, B., Zhang, J. C. and Zhang, W. T. 2016. Modification of abandoned fine blue-coke: optimization study on removal of p-nitrophenol using response surface methodology. RSC Advances, 6(16): 13537-13547.

Xiaojun, Z. M. Y. S. H. 2007. High value-added-value utilization of coke fine. Fuel & Chemical Processes, 2: 008.

Yongjun, C., Cairong, Z., Caiying, W., Xiaoman, S., Daomin, Y. and Shibin, J. 1998. Activated carbon made from semi coke powder and compared with coal based carbon. Coal Conversion, 4.

Zhang, C., Ye, D., Cui, Y., Wu, C. and Shi, X. 1999. Study on industrial test of manufacture activated carbon in waste semi-coke powder. Coal Conversion, 22(2): 75-78.