Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.25236

183 (2020) 315–324
April

Adsorption study of heavy metal ions from aqueous solution by activated carbon in single and mixed system

Chengyu Suo[a], Kang Du[b], Rongfang Yuan[a,*], Huilun Chen[a], Fei Wang[a], Beihai Zhou[a,*]

[a]*Beijing Key Laboratory of Resource-oriented Treatment of Industrial Pollutants, School of Energy and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China, emails: yuanrongfang@ustb.edu.cn (R. Yuan), zhoubeihai@sina.com (B. Zhou), 1142728357@qq.com (C. Suo) , chenhuilun@ ustb.edu.cn (H. Chen), wangfei@ustb.edu.cn (F. Wang)*
[b]*CECEP&CIECC Environmental Investment Management Co., Ltd., Beijing 100034, China, email: lang.dk@163.com*

Received 13 June 2019; Accepted 27 November 2019

ABSTRACT

Nowadays, various heavy metals have been released into the waters, causing serious pollution of water resources and endangering human health. Therefore, it is very important to study the removal of heavy metals from water. In this work, the adsorption of heavy metal ions including Pb(II), Cu(II), Zn(II), Cd(II) and Cr(VI) onto activated carbon (AC) from aqueous solutions was investigated in both single and mixed systems. The batch adsorption experiment for heavy metal ions on AC in single system was studied at different conditions including contact time, initial concentration, initial pH and adsorbent dosage. The results indicated that the adsorption kinetics and isotherms followed the pseudo-first order model and the Langmuir isotherm model, respectively. The final removal efficiencies and maximum adsorption capacity followed the order of Pb(II) > Cr(VI) > Cd(II) > Cu(II) > Zn(II) at the pH 5.0 and 25°C in single system. The adsorption of heavy metals was mainly determined by the pH of the solution and the surface properties of the adsorbent, and it was found that the initial pH of 3 was optimal for the removal of Cr(VI), which was different from the optimum initial pH of 7.0 for Pb(II), Cu(II), Zn(II) and Cd(II). The results demonstrated that the electrostatic interaction between the surface of AC and heavy metal ions played an important role in the adsorption of heavy metal ions. In addition, compared with the results in single system, the results in multi-component mixed system showed that the adsorption of Cu(II) and Cr(VI) was promoted, but the adsorption of Zn(II) and Cd(II) was inhibited. The factors affecting the adsorption impetuses are interactive involving electrostatic interaction, promotion or inhibition between heavy metal ions, chemical reaction and so on.

Keywords: Activated carbon; Heavy metal ions; Mixed system; Adsorption kinetics; Adsorption isotherms

1. Introduction

The pollution of heavy metals has become an increasingly severe environmental issue nowadays that deserves global attention [1–3]. Heavy metals are becoming increasingly used in various industries such as mining and smelting of metals, energy and fuel production, iron and steel, aerospace, electroplating and so on [4]. As one of the most important pollutants affecting water resources [5], heavy metals may cause irreversible damage to the human health and ecosystem due to its characteristics of persistence [6], accumulation, difficulty to degradation [7] and acute toxicity at both high and low concentrations [4]. In addition, heavy metals may accumulate in organisms via the biological chain [8,9]. Hence, it is imperative to remove the heavy metals during wastewater treatment.

Various technologies, including electrolysis [10], filtration [11], adsorption [12], coagulation–flocculation [13],

---

* Corresponding authors.

membrane separation [14], chemical precipitation and electrochemical precipitation [14], are available for removing heavy metals from wastewater [15]. Among these technologies, adsorption is regarded as one of the most promising strategies [16–18] because of its obvious advantages such as low cost, high efficiency, simplicity, flexibility and environmental friendliness [19,20]. According to the previous studies, a variety of adsorbents, including carbon foam [21], clay minerals [22], activated carbon (AC) [23], biochar prepared from agricultural wastes [24–26] have been widely used for removing heavy metals from wastewater. Among these adsorbents, AC is one of the most effective adsorbents for heavy metals removal because of its large specific surface area and abundant surface functional groups [27,28]. These tasks can serve for the treatment of actual wastewater characterised by complexity and emergency using AC as adsorbents [29,30].

Nowadays, many efforts have been devoted to study the removal of heavy metals in aqueous solutions by AC adsorption [31,32]. However, most studies were focused on the adsorption of single heavy metal ion, while the researches on multi-component heavy metal ions adsorption were limited [33,34]. Besides, in the existing studies on competitive adsorption of heavy metal ions, most are about binary or ternary adsorption [21,23,35]. The research of the interaction and competitive mechanism between the AC and heavy metal ions is far from sufficient [36,37]. However, few studies on the adsorption of multi-component solutions involving five heavy metal ions have been reported [29,38–40]. Hence, it is of great necessity to make further study on the competitive adsorption mechanism of multiple heavy metal ions in mixed system.

The aim of this work was to study the adsorption kinetics and competitive mechanisms of the heavy metal ions including Pb(II), Cu(II), Zn(II), Cd(II) and Cr(VI) in coexisting systems. The effects of contact time, initial concentration, initial pH and adsorbent dosage on heavy metal removal rates in both single aqueous solutions and multi-component system were discussed, providing a solid basis for the application of AC in wastewater treatments involving multiple heavy metals. In addition, the adsorption priority order, mutual interference and competition onto AC in mixed system were analyzed. This work cannot only provide a fast and efficient approach to solve the problem of treating high concentration heavy metals pollution wastewater resulting from emergency accident but also provide a valid theoretical foundation about absorption mechanism towards the applications of the AC in wastewater treatments.

2. Materials and methods

2.1. Materials and reagents

All chemical regents used in this study were of analytical grade. The regents were used without further purification. $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, $Pb(NO_3)_2$ and $K_2Cr_2O_7$ were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China), while NaOH and HNO_3 which were used for pH adjustment were bought from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Precision pH meter (PSH-3C) was bought from Shanghai INESA Scientific Instrument Co., Ltd. (Shanghai, China), electronic balance (ML 104/02) was bought from Mettler Toledo Instrument Co., Ltd. (Shanghai, China), and constant temperature oscillator (LPH-200D) was bought from labCAN Instrument Equipment Co. Ltd., (Wuxi, China). Adsorbent wooden commercial AC was supplied by Yiqing activated carbon Co., Ltd. (Jiangsu China). The stock solutions of Pb(II), Cu(II), Zn(II), Cd(II) and Cr(VI) with concentration of 1,000 mg/L were prepared by dissolving a certain amount of corresponding reagent into a 1,000 mL volumetric flask, respectively. In order to prevent the heavy metal ions from hydrolysis, the stock solutions and the working solutions diluted from the stock solutions were stored at 4°C under HNO_3 (5 wt%) condition. Deionized (DI) water and ultrapure water (conductivities <0.5 ms/cm) were used throughout the experiment obtained from Milli-Q water purification system (Millipore Synergy 185, the United States).

The AC was immersed in DI water for 24 h, washed several times after stirred to remove dust and other impurities. Then the AC were filtered and dried in an oven at 80°C for 24 h. Finally, the dried AC cooled to room temperature was powdered and sieved to particle diameter of 0.075 to 0.15 mm, stored in a desiccator until it was used.

2.2. Adsorption experiments

The adsorption processes were performed in 50 mL tubes containing a certain amount of AC and 25 mL of heavy metals solution. Then, the tubes were placed into a thermostat shaker. The adsorption experiment was conducted with the speed of 250 rpm at 25°C. The pH value of solution before and after adsorption was measured by a fixed pH-meter with regular correction. The adsorption experiments of single factor including contact time, initial concentration, initial pH and adsorbent dosage for single heavy metal ions adsorption were carried out in batch experiments. Also, the effect of dosage on adsorption performance of AC under different pH value was investigated using the multi-component solution containing Pb(II), Zn(II), Cu(II), Cd(II) and Cr(VI) with initial concentration of 25 mg/L, respectively.

The adsorption capacity (q_t) of AC and the removal percentage (R) of heavy metals were calculated using Eqs. (1) and (2) as follows, respectively.

$$q_t = \frac{\left(C_0 - C_e\right) \times V}{m} \tag{1}$$

$$R\left(\%\right) = \frac{\left(C_0 - C_e\right)}{C_0} \times 100\% \tag{2}$$

where q_t (mg/g) is the adsorption capacity at certain time; C_0 (mg/L) is the initial concentration of the heavy metals at a certain time; C_e (mg/L) is the equilibrium concentrations of the heavy metals; V (L) represents the volume of the solution and m (g) is the quality of AC; R (%) is the removal percentage.

2.3. Analytical methods

Identically, prior to measurement, all samples were separated from supernatant after adsorption, filtered through membrane filters (0.45 μm pore size, Jinteng, Tianjin Jinteng Technology Co., Ltd.), and acidified with HNO_3 (3 wt%). The residual heavy metal concentrations of all samples were measured using an inductively coupled plasma-optical emission spectrometry (ICP-OES, Thermo, 7000 plus series). All adsorption experiments were performed in triplicate with a relative standard deviation of less than 1%.

3. Results and discussions

3.1. Adsorption of single heavy metal ion

3.1.1. Adsorption kinetics

The adsorption kinetics in the single system was studied. The pseudo-first order model, pseudo-second order model and intraparticle diffusion model were used to describe the adsorption kinetics processes which are expressed as Eqs. (3)–(5) [41–44].

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{3}$$

$$q_t = \frac{k_2 q_e^2 t}{\left(1 + k_2 q_e t\right)} \tag{4}$$

$$q_t = kt^{1/2} + d \tag{5}$$

where q_t (mg/g) and q_e (mg/g) are the adsorbed capacity at a certain time and at equilibrium; k_1 and k_2 are the rate constants of the pseudo-first order and pseudo-second order models, respectively; k and d are the rate constants and adsorption constant of the intraparticle diffusion model, respectively.

The adsorption kinetics of Pb(II), Cu(II), Zn(II), Cd(II) and Cr(VI) by AC are shown in Fig. 1. The trends of adsorption process for different heavy metal ions were similar. It can be seen intuitively from Fig. 1 that more than 80% of the adsorption capacity was achieved in the first 5 min for all of the heavy metal ions, which corresponded to the rapid adsorption stage. The adsorption rates all slowed down as the residual concentration and adsorption sites in solutions were decreased. Adsorption equilibriums were reached in 30 min eventually, and the removal rates after equilibrium for the above mentioned heavy metal ions followed the order of Pb(II) > Cr(VI) > Cd(II) > Cu(II) > Zn(II). In order to compare the adsorption performance of heavy metal ions on AC, three kinetic models were employed to correlate the adsorption data. As the fitting parameters calculated by linear regression analysis are listed in Table 1, the pseudo-second order model is far superior to the pseudo-first order model and intraparticle diffusion model according to the perspective of fitting parameters (R^2). It suggests that the adsorption was a chemisorption process occurred between AC and heavy metal ions [45]. The chemisorption could be attributed to the complexation reaction [36]. Thus, the interaction between these heavy metal ions and functional groups of AC is the key adsorption power [26].

The adsorption capacities of the adsorption equilibrium were 25.3, 7.5, 4.2, 8.8 and 9.3 mg/g for Pb(II), Cu(II), Zn(II), Cd(II) and Cr(VI) at pH of 5.0, respectively. On the basis of kinetic rate constants, fast absorption properties of five heavy metal ions on AC could be deduced. These results can be attributed to the active absorption sites on the surface of the AC, which has good prospects for the rapid removal of heavy metal ions from wastewater.

3.1.2. Adsorption isothermals

The adsorption isotherm study was conducted for the above mentioned five heavy metal ions with different initial concentrations at 25°C and the adsorption time was 120 min. The results were analyzed using Langmuir and Freundlich models described by Eqs. (6) and (7), respectively [41–44].

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{6}$$

$$q_e = K_F C_e^{1/n} \tag{7}$$

where q_e (mg/g) and q_m (mg/g) are the adsorption capacity at equilibrium and the theoretically maximum adsorption capacity, respectively; K_L (L/mg) is the constant of Langmuir model related to the energy of adsorption; K_F is the parameter of Freundlich model, which predicts the amount of the heavy metals per unit mass of adsorbent at equilibrium; C_e (mg/L) is the concentration of residual heavy metal in aqueous solution at equilibrium; n is a parameter of Freundlich model related to the adsorption effectiveness.

It can be easily seen from Fig. 2 that the adsorption capacity of the five heavy metal ions on the AC increased and the increase rate slowed down with the increase of the initial concentration. It demonstrates that AC is especially suitable for heavy metal ions aqueous solution with high concentration. The fitting parameters of the two isotherm models estimated by linear regression analysis are listed in Table 2. According to the comparison of parameter (R^2), the adsorptions of five heavy metal ions are all more consistent with Langmuir isotherm model rather than Freundlich isotherm model. It revealed that the adsorption processes follow a monolayer reaction and the even adsorption sites on the surface control the adsorption processes [46]. In addition, it can be seen that the order of saturated adsorption capacities (q_e) of AC followed Pb(II) (34.7 mg/g) > Cr(VI) (26.6 mg/g) > Cd(II) (10.8 mg/g) > Cu(II) (8.8 mg/g) > Zn(II) (4.4 mg/g), which was consistent with the kinetic results above completely. It reflects the adsorption diversity and preference for different heavy metal pollutants due to the huge gap between the adsorption capacity of AC for different heavy metal ions [38], which provides a theoretical basis for competitive adsorption.

3.1.3. Effects of the AC dosage

The adsorbent dosage is an important parameter because it has a large effect on the removal and capacity of AC at a certain initial concentration of heavy metal ions [47]. Fig. 3 shows the effect of AC dosage from 0.4 to 10 g/L on adsorption of heavy metal ions on adsorption capacity and removal rate. It is clear that with the increase of dosage, the removal rate was obviously increased from Fig. 3a, but the adsorption capacity was significantly decreased from Fig.

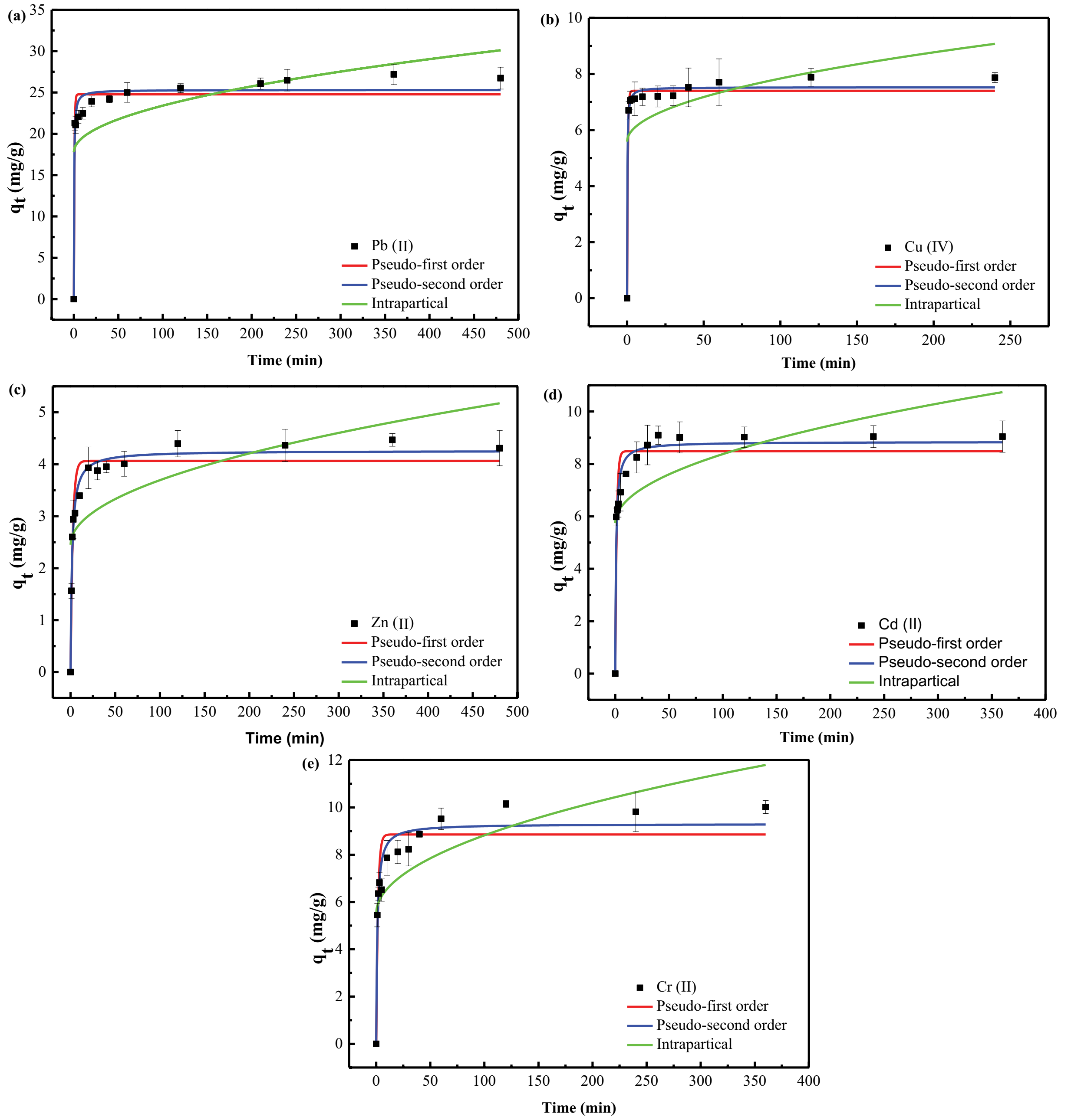

Fig. 1. Adsorption kinetics of heavy metal ions: (a) Pb(II), (b) Cu(II), (c) Zn(II), (d) Cd(II) and (e) Cr(VI) on AC in single system (initial concentration 25 mg/L, pH 5.0, temperature 25°C).

Table 1
Fitting parameters of adsorption kinetic using different models at 25°C and pH of 5.0 in the single systems

Heavy metal ions	Pseudo-first order			Pseudo-second order			Intraparticle diffusion		
	q_e	k_1	R^2	q_e	k_2	R^2	k	d	R^2
Pb(II)	24.770	1.695	0.930	25.300	0.136	0.960	0.562	17.700	0.282
Cu(II)	7.399	2.272	0.979	7.527	0.927	0.987	0.225	5.585	0.155
Zn(II)	4.065	0.418	0.936	4.261	0.146	0.981	0.124	2.452	0.431
Cd(II)	8.486	0.762	0.885	8.843	0.147	0.961	0.263	5.738	0.323
Cr(VI)	8.856	0.620	0.849	9.303	0.932	0.930	0.332	5.500	0.465

3b. This is mainly related to the number and the density of active adsorption sites which are related to dosage of the AC in the aqueous solution [5]. At low dosage of AC, it was faster to reach saturation and larger of adsorption capacity due to all surface sites exposed to heavy metal ions [48,49]. The increased dosage of AC greatly promotes the number and density of the adsorption sites, thereby increasing the removal rate [5]. However, it leads to a non-proportional increase in the effective active sites, resulting in the reduction of the utilization rate and the adsorption capacity.

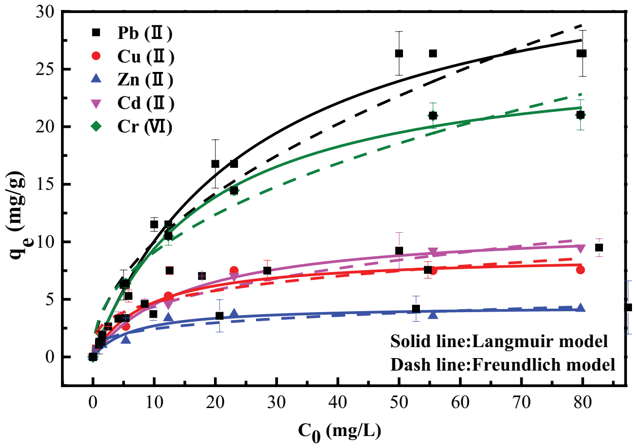

Fig. 2. Adsorption isothermals of Pb(II), Cu(II), Zn(II), Cd(II) and Cr(VI) on AC. (pH 5.0, temperature 25°C).

3.1.4. Effect of initial pH on adsorption of heavy metals

Initial pH has been identified as a critical condition affecting the water–adsorbent interface adsorption process [50]. The effect of initial pH ranging from 2 to 10 on the adsorption property for Pb(II), Cu(II), Zn(II), Cd(II) and Cr(VI) on AC was investigated, and the absorption results are shown in Fig. 4.

The removal rate of five heavy metal ions was significantly affected by the initial pH. For heavy metal ions of Pb(II), Cu(II), Zn(II) and Cd(II), the removal rate was relatively low and its growth trend is relatively slow at the pH of 2.0–3.0 for Pb(II) and Cu(II) and pH 2.0–4.0 for Cd(II) and Zn(II). However, the removal rate dramatically increased accordingly as the pH increased at higher pH, especially at the pH 5.0–6.0 for Pb(II) and Cu(II) and pH 6.0–7.0 for Cd(II) and Zn(II). The adsorption trends of initial pH were consistent with the previous reports. This phenomenon was related to the charge on the surface of the adsorbent [51,52]. At lower pH, protonated functional groups of AC caused by high concentration of H^+ leads to a positively charged

Table 2
Fitting parameters of the Langmuir and Freundlich models at 25°C and pH of 5.0 in the single systems

Heavy metal ions	Langmuir			Freundlich		
	q_m	K_L	R^2	K_F	n	R^2
Pb(II)	34.715	0.049	0.991	3.745	2.139	0.953
Cu(II)	8.818	0.220	0.956	2.648	3.376	0.828
Zn(II)	4.399	0.402	0.976	1.835	4.748	0.861
Cd(II)	10.816	0.101	0.996	2.186	2.849	0.958
Cr(VI)	26.635	0.055	0.996	3.281	2.258	0.967

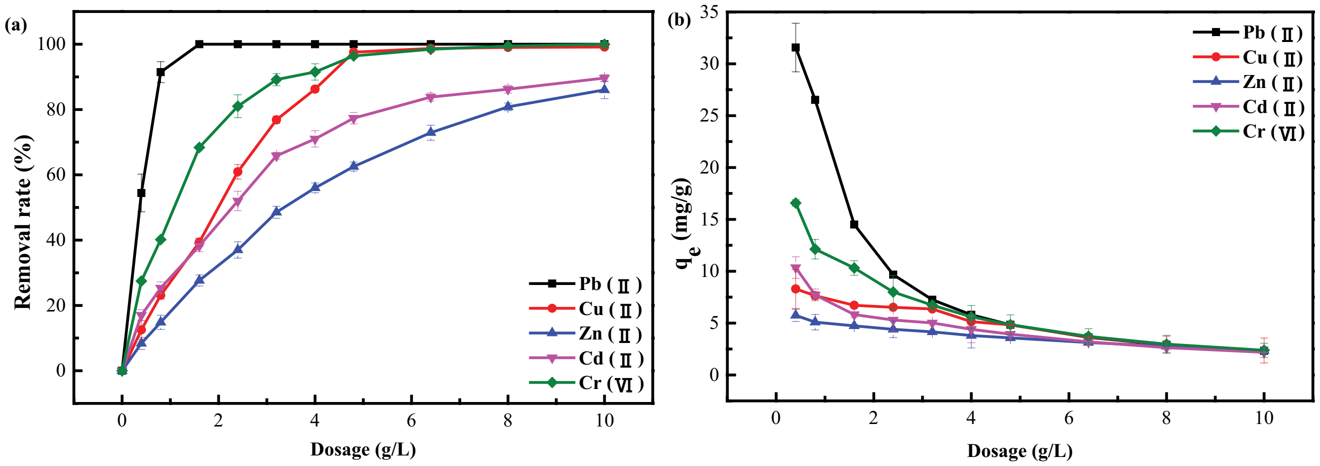

Fig. 3. Effect of (a) removal and (b) q_e of dosage on Pb(II), Cu(II), Zn(II), Cd(II) and Cr(VI) adsorption efficiency on AC (initial concentration 25 mg/L, pH 5.0, temperature 25°C).

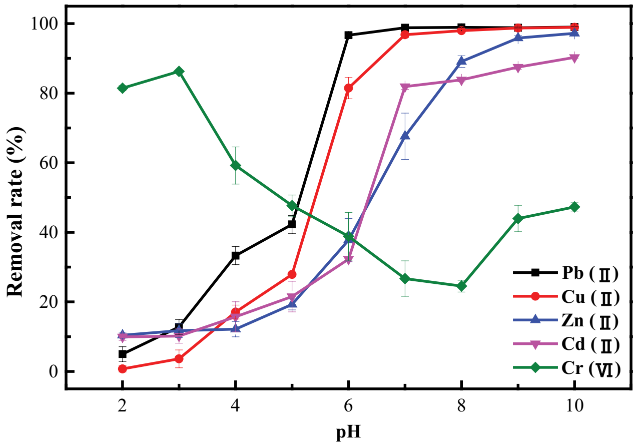

Fig. 4. Effect of pH on the adsorption rate of Pb(II), Cu(II), Zn(II), Cd(II) and Cr(VI) adsorption on AC (initial concentration 25 mg/L, temperature 25°C).

interface [49]. AC repels the same positively charged heavy metal cation due to the electrostatic interaction between the surface of AC and the heavy metals. In addition, the competition among protonated functional groups and heavy metal cations for active site impair absorption capacity [26]. With the increase of initial pH, the positive charge on the surface of the functional groups decreases first due to neutralization resulting in the decrease in electrostatic repulsion. And then the negative charge increases due to the accumulation of hydroxide ions (OH^-), resulting in enhanced electrostatic attraction and weakening the protonation of the AC surface thereby enhancing adsorption ability of heavy metal cations [49]. Other than that, a large amount of hydroxide ions cause heavy metal cations to reach the limit of the concentration required for the solubility product constant, thereby increasing the removal rate of heavy metals [5].

It can be seen from Fig. 4 that the removal rate curve of heavy metal anion $Cr_2O_7^{2-}$ shape a horizontal type "S" with the increase of pH, and the removal rate was higher under acidic conditions, but lower under alkaline conditions. The effect of pH on adsorption for $Cr_2O_7^{2-}$ can also be explained by the electrostatic interaction between the surface charge of AC and heavy metal ions in solution, but $Cr_2O_7^{2-}$ presents as an anion has an opposite interaction compared with the influence mechanisms of four cations described above [53].

In addition, the ionic state of heavy metals in aqueous solution varies greatly under different pH conditions due to the complexation of heavy metal ions with hydrogen ions (H^+) or hydroxide ions (OH^-) based on previous reports [12]. Adsorption mechanisms for different ionic states of heavy metals differ greatly on the active site of AC, resulting in differences in adsorption capacity under different pH conditions.

3.2. *Adsorption of multi-component heavy metal ions*

In order to obtain a deeper understanding of the adsorption efficiency and competition between heavy metal ions, adsorption experiment was performed in DI water of multicomponent mixed system containing Pb(II), Cu(II), Zn(II), Cd(II) and Cr(VI), and the results are shown in Fig. 5. It can be seen that the removal rate of Pb(II) had almost reached 100% under the condition of zero dosage, so it can be proved that Pb(II) could not coexist with other four heavy metal ions in this system. Because Pb(II) mainly reacted chemically with $Cr_2O_7^{2-}$ or CrO_4^{2-} to yellow precipitate [54].

The optimum pH was still 3.0 in mixed system, which was consistent with that of the single heavy metal adsorption mentioned above. It can be seen from Fig. 5b that the removal rate of Cr(VI) reached approximately 100% at pH 3.0 with the AC dosage of 3.2 g/L, which was much higher than the removal rate in single heavy metal system under the same conditions. Besides, the removal rate of Cr(VI) in mixed system was also higher than that in single system at the same dosage from Figs. 3 and 5b. The results indicates that the other three heavy metals promote the adsorption of Cr(VI) [55]. From Figs. 5b–e, the removal rate decreased for Cr(VI) but increased for Cu(II), Zn(II) and Cd(II) under the same dosage with the increase of pH. The reason is that as the pH increases, the electrostatic repulsion between heavy metal cations of Cu(II), Zn(II) and Cd(II) and the charge on the surface of the AC and the electrostatic attraction for Cr(VI) are weakened, and the promotion for Cr(VI) by heavy metal cations is weaker than the reduction of electrostatic forces [26,56]. From Figs. 5b–j, more AC was required to achieve removal rate for Cr(VI) to 100% with the increase of the pH value. In particular, from Figs. 5h–j, the removal rate of Cr(VI) cannot be achieved 100% any more, and the initial amount of precipitation without AC increased at higher pH, resulting in the reaction of Cu(II), Zn(II) and Cd(II) with more amount of CrO_4^{2-}. However, although more amounts of CrO_4^{2-} present in the mixed composite system, the other four metals are nearly precipitated completely due to the accumulation of a large amount of hydroxide (OH^-), the opposite tendency of the initial precipitation amount for Cr(VI) could be seen from Figs. 5h–j.

From Figs. 3 and 5e, the removal efficiency of Cu(II) in single system was higher than that in the mixed system at pH of 5.0 and dosage range from 0 to 10 mg/L, and the removal efficiency of Cd(II) and Cd(II) was lower under the same conditions. Similarly, from Figs. 4 and 5a–j, the removal efficiency of Cu(II) in single system was higher than that in the mixed system at dosage of 0.8 mg/L and pH range from 2.0 to 10.0, and the removal efficiency of Zn(II) and Cd(II) was lower under the same conditions. The adsorption isotherm study was conducted for the above mentioned five heavy metal ions with different initial concentrations at 25°C at pH of 3.0, 5.0 and 8.0. According to the comparison of parameter (R^2), the adsorptions of four heavy metal ions (except Pb(II)) were all more consistent with Langmuir isotherm model rather than Freundlich isotherm model. And the fitting parameter q_m of the Langmuir model estimated by linear regression analysis is listed in Table 3. Compared with the parameters from Table 2 in single system, the adsorption capacity of Cr(VI) and Cu(II) was higher but the adsorption capacity of Zn(II) and Cd(II) was lower conversely in the mixed system. And the results under the condition of pH of 3.0 and 8.0 are consistent with the conclusions above. Therefore, the adsorption of Cr(VI) and Cu(II) was promoted but the adsorption of Zn(II) and Cd(II) was suppressed conversely in the mixed system and the inhibition is weakened as the pH increases

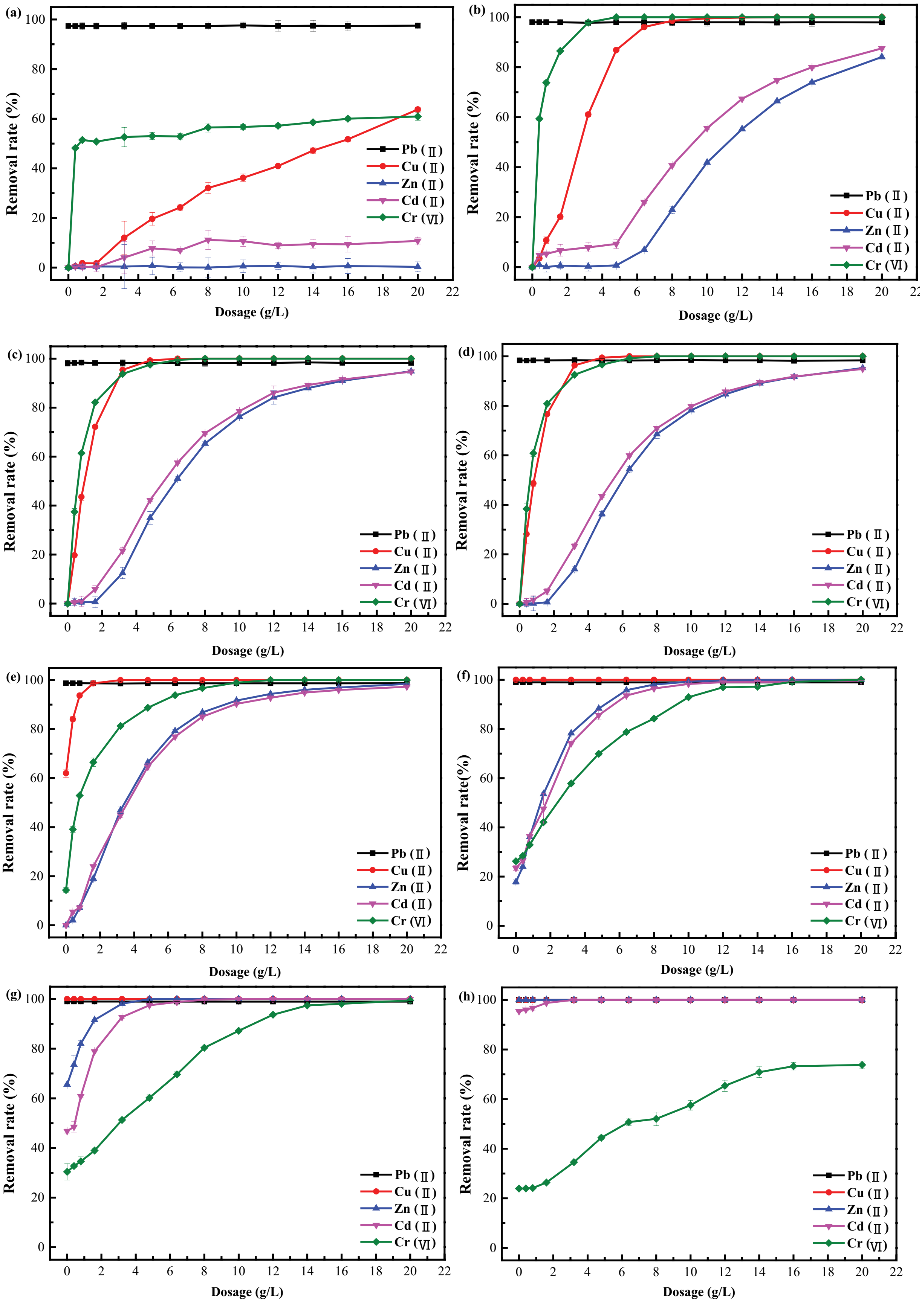

Fig. 5. Continued

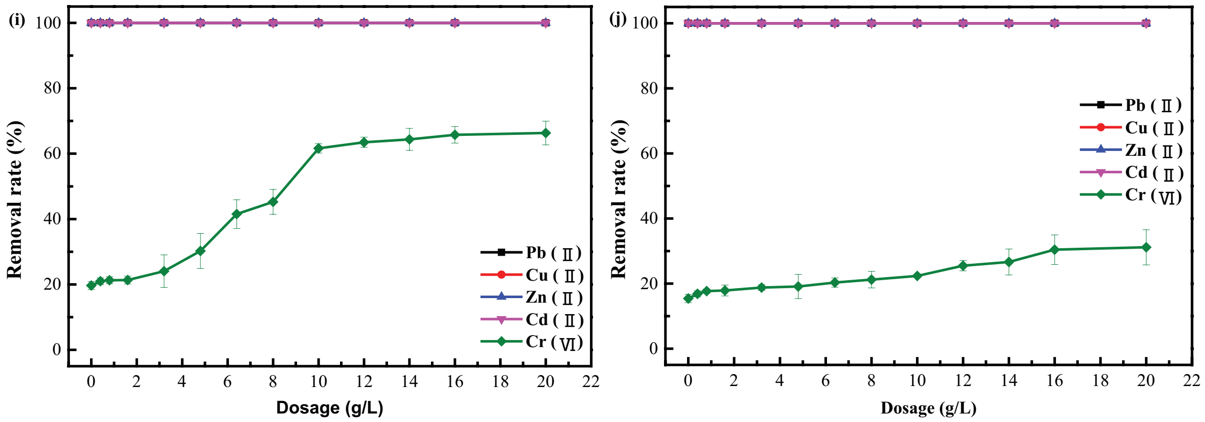

Fig. 5. Effects of the dosage on the adsorption of Pb(II), Cu(II), Zn(II), Cd(II) and Cr(VI) on AC under different pH: (a) 2.0, (b) 3.0, (c) 4.0, (d) 5.0, (e) 6.0, (f) 7.0, (g) 8.0, (h) 9.0, (i) 10.0, (j) 11.0 (initial concentration 25 mg/L, temperature 25°C).

Table 3
Fitting parameter q_m of the Langmuir model at 25°C and pH of 3.0, 5.0 and 8.0 in the mixed systems

Items	Pb(II)	Cu(II)	Zn(II)	Cd(II)	Cr(VI)
pH of 3.0	/	5.697	1.088	2.021	43.991
pH of 5.0	/	20.439	2.109	3.495	32.686
pH of 8.0	/	35.722	29.985	22.363	15.245

compared with the results in single system. Because more hydroxide precipitates were produced at higher pH, and the concentration of heavy metal ions involved in competitive adsorption was lower resulting in the removal rate of Zn(II) and Cd(II) closer to the data in a single system under the same condition [21].

4. Conclusion

The adsorption of Pb(II), Cu(II), Zn(II), Cd(II) and Cr(VI) in single system conforms to the pseudo-first order model and the Langmuir isotherm model, and the final removal efficiencies followed the order of Pb(II) > Cr(VI) > Cd(II) > Cu(II) > Zn(II) at the pH 5.0 and 25°C in single system. The optimum pH is 3.0 for Cr(VI) and the optimum pH is 7.0 for Pb(II), Cu(II), Zn(II) and Cd(II). The adsorption process was mainly affected by the pH of the solution due to its effect on the surface charge of the AC and the ion state in the aqueous solution. The adsorption in mixed system shows that Pb(II) cannot coexist in this system, and the removal rates of Cu(II) and Cr(VI) were promoted, the removal rates of Zn(II) and Cd(II) were inhibited. In addition, the driving force of adsorption is affected by a combination of factors involving electrostatic interaction, promotion or inhibition between heavy metal ions, chemical reaction and so on. This work is expected not only to provide effective guidance for the application of AC in the actual complex wastewater treatment involving various heavy metal pollutants in the future but also provide a valid theoretical foundation about absorption mechanism towards the applications of the AC in wastewater treatments.

Acknowledgement

This work was supported by National Science and Technology Major Project of China (2017ZX07107-005).

References

[1] A. Alahabadi, H. Malvandi, Contamination and ecological risk assessment of heavy metals and metalloids in surface sediments of the Tajan River, Iran. Mar. Pollut. Bull., 133 (2018) 741–749.
[2] M.G. Kiran, K. Pakshirajan, G. Das, Heavy metal removal from multicomponent system by sulfate reducing bacteria: mechanism and cell surface characterization, J. Hazard. Mater., 324 (2017) 62–70.
[3] Y. Wu, H. Pang, Y. Liu, X. Wang, S. Yu, D. Fu, J. Chen, X. Wang, Environmental remediation of heavy metal ions by novel-nanomaterials: a review, Environ. Pollut., 246 (2019) 608–620.
[4] T.A.H. Nguyen, H.H. Ngo, W.S. Guo, J. Zhang, S. Liang, Q.Y. Yue, Q. Li, T.V. Nguyen, Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater, Bioresour. Technol., 148 (2013) 574–585.
[5] E. Da'na, A. Awad, Regeneration of spent activated carbon obtained from home filtration system and applying it for heavy metals adsorption, J. Environ. Chem. Eng., 5 (2017) 3091–3099.
[6] M. Bilal, J.A. Shah, T. Ashfaq, S.M. Gardazi, A.A. Tahir, A. Pervez, H. Haroon, Q. Mahmood, Waste biomass adsorbents for copper removal from industrial wastewater--a review, J. Hazard. Mater., 263 (2013) 322–333.
[7] W. Zhang, H. Feng, J. Chang, J. Qu, H. Xie, L. Yu, Heavy metal contamination in surface sediments of Yangtze River intertidal zone: an assessment from different indexes, Environ. Pollut., 157 (2009) 1533–1543.
[8] L. Li, F. Zhu, Y. Lu, J. Guan, Synthesis, adsorption and selectivity of inverse emulsion Cd (II) imprinted polymers, J. Chem. Eng., 26 (2018) 494–500.
[9] G. Xiao, X. Zhang, H. Su, T. Tan, Plate column biosorption of Cu(II) on membrane-type biosorbent (MBS) of Penicillium biomass: optimization using statistical design methods, Bioresour. Technol., 143 (2013) 490–498.
[10] X. Deng, L. Lu, H. Li, F. Luo, The adsorption properties of Pb (II) and Cd (II) on functionalized graphene prepared by electrolysis method, J. Hazard. Mater., 183 (2010) 923–930.
[11] Y. Cui, Q. Ge, X.Y. Liu, T.S. Chung, Novel forward osmosis process to effectively remove heavy metal ions, J. Membr. Sci., 467 (2014) 188–194.
[12] J.B. Dima, C. Sequeiros, N.E. Zaritzky, Hexavalent chromium removal in contaminated water using reticulated chitosan micro/nanoparticles from seafood processing wastes, Chemosphere, 141 (2015) 100–111.

[13] T.A. Kurniawan, G.Y.S. Chan, W. H. Lo, S. Babel, Physico-chemical treatment techniques for wastewater laden with heavy metals, Chem. Eng. J., 118 (2006) 83–98.

[14] A. Kolbasov, S. Sinha-Ray, A.L. Yarin, B. Pourdeyhimi, Heavy metal adsorption on solution-blown biopolymer nanofiber membranes, J. Membr. Sci., 530 (2017) 250–263.

[15] Y. Ahmadi, S.E. Eshraghi, P. Bahrami, M. Hasanbeygi, Y. Kazemzadeh, A. Vahedian, Comprehensive Water-Alternating-Gas (WAG) injection study to evaluate the most effective method based on heavy oil recovery and asphaltene precipitation tests, J. Pet. Sci. Eng., 133 (2015) 123–129.

[16] C.M. Park, D. Wang, J. Han, J. Heo, C. Su, Evaluation of the colloidal stability and adsorption performance of reduced graphene oxide-elemental silver/magnetite nanohybrids for selected toxic heavy metals in aqueous solutions, Appl. Surf. Sci., 471 (2019) 8–17.

[17] P. Tan, J. Sun, Y. Hu, Z. Fang, Q. Bi, Y. Chen, J. Cheng, Adsorption of Cu^{2+}, Cd^{2+} and Ni^{2+} from aqueous single metal solutions on graphene oxide membranes, J. Hazard. Mater., 297 (2015) 251–260.

[18] P. Tan, Y. Hu, Q. Bi, Competitive adsorption of Cu^{2+}, Cd^{2+} and Ni^{2+} from an aqueous solution on graphene oxide membranes, Colloids Surf. A, 509 (2016) 56–64.

[19] C.G. Lee, M.K. Song, J.C. Ryu, C. Park, J.W. Choi, S.H. Lee, Application of carbon foam for heavy metal removal from industrial plating wastewater and toxicity evaluation of the adsorbent, Chemosphere, 153 (2016) 1–9.

[20] M. Tuzen, M. Soylak, Multi-element coprecipitation for separation and enrichment of heavy metal ions for their flame atomic absorption spectrometric determinations, J. Hazard. Mater., 162 (2009) 724–729.

[21] C.G. Lee, S. Lee, J.A. Park, C. Park, S.J. Lee, S.B. Kim, B. An, S.T. Yun, S.H. Lee, J. W. Choi, Removal of copper, nickel and chromium mixtures from metal plating wastewater by adsorption with modified carbon foam, Chemosphere, 166 (2017) 203–211.

[22] C. Chen, X. Yang, J. Wei, X. Tan, X. Wang, Eu(III) uptake on rectorite in the presence of humic acid: a macroscopic and spectroscopic study, J. Colloid Interface Sci., 393 (2013) 249–256.

[23] D. Eeshwarasinghe, P. Loganathan, S. Vigneswaran, Simultaneous removal of polycyclic aromatic hydrocarbons and heavy metals from water using granular activated carbon, Chemosphere, 223 (2019) 616–627.

[24] F. Lian, G. Cui, Z. Liu, L. Duo, G. Zhang, B. Xing, One-step synthesis of a novel N-doped microporous biochar derived from crop straws with high dye adsorption capacity, J. Environ. Manage., 176 (2016) 61–68.

[25] B. Sarkar, S. Mandal, Y.F. Tsang, P. Kumar, K.H. Kim, Y.S. Ok, Designer carbon nanotubes for contaminant removal in water and wastewater: a critical review, Sci. Total Environ., 612 (2018) 561–581.

[26] F. Cao, C. Lian, J. Yu, H. Yang, S. Lin, Study on the adsorption performance and competitive mechanism for heavy metal contaminants removal using novel multi-pore activated carbons derived from recyclable long-root *Eichhornia crassipes*, Bioresour. Technol., 276 (2019) 211–218.

[27] H. Guedidi, L. Reinert, J. M. Lévêque, Y. Soneda, N. Bellakhal, L. Duclaux, The effects of the surface oxidation of activated carbon, the solution pH and the temperature on adsorption of ibuprofen, Carbon, 54 (2013) 432–443.

[28] J. Shen, G. Huang, C. An, X. Xin, C. Huang, S. Rosendahl, Removal of Tetrabromobisphenol A by adsorption on pinecone-derived activated charcoals: synchrotron FTIR, kinetics and surface functionality analyses, Bioresour. Technol., 247 (2018) 812–820.

[29] A.R. Kaveeshwar, P.S. Kumar, E.D. Revellame, D.D. Gang, M.E. Zappi, R. Subramaniam, Adsorption properties and mechanism of barium (II) and strontium (II) removal from fracking wastewater using pecan shell based activated carbon, J. Clean. Prod., 193 (2018) 1–13.

[30] H.A. Hegazi, Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents, HBRC J., 9 (2013) 65–76.

[31] A. Ozcan, A.S. Ozcan, S. Tunali, T. Akar, I. Kiran, Determination of the equilibrium, kinetic and thermodynamic parameters of adsorption of copper (II) ions onto seeds of *Capsicum annuum*, J. Hazard. Mater., 124 (2005) 200–208.

[32] S. Tunali Akar, A. Gorgulu, T. Akar, S. Celik, Decolorization of Reactive Blue 49 contaminated solutions by *Capsicum annuum* seeds: batch and continuous mode biosorption applications, Chem. Eng. J., 168 (2011) 125–133.

[33] V. Nejadshafiee, M.R. Islami, Adsorption capacity of heavy metal ions using sultone-modified magnetic activated carbon as a bio-adsorbent, Mater. Sci. Eng. C, 101 (2019) 42–52.

[34] L.Y. Li, X. Gong, O. Abida, Waste-to-resources: exploratory surface modification of sludge-based activated carbon by nitric acid for heavy metal adsorption, Waste Manage., 87 (2019) 375–386.

[35] X. Luo, Z. Zhang, P. Zhou, Y. Liu, G. Ma, Z. Lei, Synergic adsorption of acid blue 80 and heavy metal ions (Cu^{2+}/Ni^{2+}) onto activated carbon and its mechanisms, J. Ind. Eng. Chem., 27 (2015) 164–174.

[36] I.A. Aguayo-Villarreal, A. Bonilla-Petriciolet, R. Muñiz-Valencia, Preparation of activated carbons from pecan nutshell and their application in the antagonistic adsorption of heavy metal ions, J. Mol. Liq., 230 (2017) 686–695.

[37] J. Valentin-Reyes, R.B. Garcia-Reyes, A. Garcia-Gonzalez, E. Soto-Regalado, F. Cerino-Cordova, Adsorption mechanisms of hexavalent chromium from aqueous solutions on modified activated carbons, J. Environ. Manage., 236 (2019) 815–822.

[38] H. Xu, H. Yuan, J. Yu, S. Lin, Study on the competitive adsorption and correlational mechanism for heavy metal ions using the carboxylated magnetic iron oxide nanoparticles (MNPs-COOH) as efficient adsorbents, Appl. Surf. Sci., 473 (2019) 960–966.

[39] L. Wang, Y. Wang, F. Ma, V. Tankpa, S. Bai, X. Guo, X. Wang, Mechanisms and reutilization of modified biochar used for removal of heavy metals from wastewater: a review, Sci. Total Environ., 668 (2019) 1298–1309.

[40] R. Tovar-Gómez, M.D.R. Moreno-Virgen, J. Moreno-Pérez, A. Bonilla-Petriciolet, V. Hernández-Montoya, C.J. Durán-Valle, Analysis of synergistic and antagonistic adsorption of heavy metals and acid blue 25 on activated carbon from ternary systems, Chem. Eng. Res. Des., 93 (2015) 755–772.

[41] E.S. Dragan, D. Humelnicu, M.V. Dinu, R.I. Olariu, Kinetics, equilibrium modeling, and thermodynamics on removal of Cr (VI) ions from aqueous solution using novel composites with strong base anion exchanger microspheres embedded into chitosan/poly(vinyl amine) cryogels, Chem. Eng. J., 330 (2017) 675–691.

[42] L. Vafajoo, R. Cheraghi, R. Dabbagh, G. McKay, Removal of cobalt (II) ions from aqueous solutions utilizing the pre-treated 2-Hypnea Valentiae algae: equilibrium, thermodynamic, and dynamic studies, Chem. Eng. J., 331 (2018) 39–47.

[43] A. Naghizadeh, R. Nabizadeh, Removal of reactive blue 29 dye by adsorption on modified chitosan in the presence of hydrogen peroxide[J], Environ. Protect. Eng., 42 (2016) 149–168.

[44] A. Mohseni-Bandpi, D.J. Elliott, M.A. Zazouli, Biological nitrate removal processes from drinking water supply-a review[J], J. Environ. Sci. Eng., 11 (2013) 35–35.

[45] M.R. Awual, M.A. Shenashen, T. Yaita, H. Shiwaku, A. Jyo, Efficient arsenic (V) removal from water by ligand exchange fibrous adsorbent, Water Res., 46 (2012) 5541–5550.

[46] S. Hena, Removal of chromium hexavalent ion from aqueous solutions using biopolymer chitosan coated with poly 3-methyl thiophene polymer, J. Hazard. Mater., 181 (2010) 474–479.

[47] M.M. Rao, A. Ramesh, G.P. Rao, K. Seshaiah, Removal of copper and cadmium from the aqueous solutions by activated carbon derived from *Ceiba pentandra* hulls, J. Hazard. Mater., 129 (2006) 123–129.

[48] E.E. ElSayed, Natural diatomite as an effective adsorbent for heavy metals in water and wastewater treatment (a batch study), Water Sci., 32 (2019) 32–43.

[49] J. Sun, M. Li, Z. Zhang, J. Guo, Unravelling the adsorption disparity mechanism of heavy-metal ions on the biomass-derived hierarchically porous carbon, Appl. Surf. Sci., 471 (2019) 615–620.

[50] X. Cai, J. He, L. Chen, K. Chen, Y. Li, K. Zhang, Z. Jin, J. Liu, C. Wang, X. Wang, A 2D-g-C3N4 nanosheet as an eco-friendly adsorbent for various environmental pollutants in water, Chemosphere, 171 (2017) 192–201.

[51] J. Sun, Z. Zhang, J. Ji, M. Dou, F. Wang, Removal of Cr^{6+} from wastewater via adsorption with high-specific-surface-area nitrogen-doped hierarchical porous carbon derived from silkworm cocoon, Appl. Surf. Sci., 405 (2017) 372–379.

[52] M. Bansal, D. Singh, V.K. Garg, A comparative study for the removal of hexavalent chromium from aqueous solution by agriculture wastes' carbons, J. Hazard. Mater., 171 (2009) 83–92.

[53] G. Xiao, Y. Wang, S. Xu, P. Li, C. Yang, Y. Jin, Q. Sun, H. Su, Superior adsorption performance of graphitic carbon nitride nanosheets for both cationic and anionic heavy metals from wastewater, J. Chem. Eng., 27 (2019) 305–313.

[54] D. Jensen, A. Ledin, T. Christensen, W.A. Wenzel, Speciation of heavy metals in landfill-leachate polluted groundwater, Water Res., 33 (1999) 2642–2650.

[55] M.F.N. Secondes, V. Naddeo, V. Belgiorno, F. Ballesteros Jr., Removal of emerging contaminants by simultaneous application of membrane ultrafiltration, activated carbon adsorption, and ultrasound irradiation, J. Hazard. Mater., 264 (2014) 342–349.

[56] C.B. Godiya, X. Cheng, D. Li, Z. Chen, X. Lu, Carboxymethyl cellulose/polyacrylamide composite hydrogel for cascaded treatment/reuse of heavy metal ions in wastewater, J. Hazard. Mater., 364 (2019) 28–38.