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ARTICLE TYPE

A preliminary investigation of the mechanism of hexavalent chromium removal by corn-bran residue and derived chars

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In this study, biochars were prepared from corn-bran residue (CBR) at low pyrolysis temperatures range from 300 to 600°C. The CBR and CBR-derived chars were characterized and utilized to remove Cr(VI) from aqueous solutions. CBR-char produced at higher temperatures has larger specific surface area and lower content of functional groups. The Cr(VI) removals by CBR and CBR-chars were mainly achieved by the reduction from Cr(VI) to Cr(III) through SO_3^{2-} or oxygen-containing functional groups from these adsorbents. The amount of Cr(VI) removed by the adsorbents ranged from 8.18 to 86.49 mg g^{-1} at the initial Cr(VI) concentration range of 50-500 mg L^{-1} (pH 2). The SO_3^{2-}-rich CBR was demonstrated to be more economical and effective for Cr(VI) removal than others, with the Cr(VI) removal efficiency of 96.02%. The results can be modeled by Freundlich isotherm at pH 2, indicating that the Cr(VI) adsorption process was complex and related with solution pH and adsorbent properties. Reduction-coupled with adsorption was the mechanism of Cr(VI) removal by CBR and CBR-derived chars.

Introduction

Increasing amounts of industrial wastewater with toxic heavy metals is being discharged, posing higher environmental risks and health harm for human, animals and plant growth. From an eco-toxicological point of view, one of the contaminants, chromium, is widely detected in chromate manufacturing, leather tanning, wood preservation, and electroplating industries,[1] existing in hexavalent (Cr(VI)) and trivalent (Cr(III)) forms generally. Cr(VI) is much more soluble and mobile in aqueous solutions than Cr(III), particularly its carcinogenic, mutagenic and teratogenic effects on biologic chain. Therefore, the development of methods for effectively removing harmful Cr(VI) from wastewater and polluted environmental matrices becomes extremely urgent.[2] A great number of treatment technologies aimed at Cr(VI) removal have been employed for wastewater purification, including ion exchange,[3] chemical precipitation,[4] membrane separation,[5] bioaccumulation[1] and adsorption. However, they are all commonly high costs or generate secondary pollution like sludge disposal problems. Consequently, disposal processes with low costs and environment ally adsorbents are exactly needed. Adsorbents such as corn residues, rice husk and straw, and chars derived from them, have been investigated recently,[6-8] with a potential to meet this demand of removing toxic heavy metals from wastewaters.

Crop residues and their carbonaceous derivatives have been suggested as cost-effective scavengers for removing Cr(VI) from waste water.[7] Crop residues that are available wastes from agricultural production and corn-starch process, can be pyrolyzed to produce biochars in the absence of oxygen or limited oxygen.[9] Although biochar properties depend mainly on feedstock source and pyrolysis temperature,[10] the optimum temperature largely relies on biochar intended application.[11] Biochars produced at low temperatures are suitable for agricultural uses, while higher temperatures can improve their porosity and then enhance the capability in adsorbing contaminants.[11] As for the Cr(VI) removal efficiency, crop residues and their carbonaceous derivatives can provide an abundant source of low-cost adsorbents for Cr(VI) removal, which is a promising technology for wastewater treatment.[6,7] Some crop residues and derived chars are comparable to activated carbons or other commercial adsorbents in terms of Cr(VI) removal capacity.[12] Additionally, the produced chars from them are cheaper than activated carbon since biochars are generally obtained at lower temperatures and without further activation process.[13] The Cr(VI) removal capacity of a given adsorbent mainly depends on reaction time, solution pH, temperature, initial Cr(VI) concentration, and material dosage.[7] Although biochar modifications can improve their affiliations to negatively charged ions,[14] which can enhance the Cr(VI) removal capacity of activated carbons, some of them require complicated and costly modification processes. Interestingly, it seems that the maximal Cr(VI) removal capacity of coconut coir was found as 27 or 70.4 mg g^{-1},[7, 15] and biochars derived from rice straw without any activation treatment showed a maximum Cr(VI) removal of 96 mg g^{-1}.[16] Many results concerning the Cr(VI) removal efficiency of new crop residues and their derivatives are frequently found in previous studies, however, limited knowledge has been acquired for a reliable selection of new materials for Cr(VI) removal simply based on the surface and structural properties.[7] In addition, the mechanisms of Cr(VI) removal by crop residues and their carbonaceous derivatives have remained

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controversial.[7] Some studies pointed out that the anionic adsorption coupled with the reduction of Cr(VI) to Cr(III) by crop residues and their derived chars likely contributed to Cr(VI) removal levels.[7, 17] The reaction mechanisms must be deeply addressed because they play important roles in the remediation of Cr(VI) pollution through using crop residues and their derived chars. Corn-bran residue (CBR) is a by-product in the starch-sugar industry, consisting of fiber and starch, and a small amount of sulfite ion (SO_3^{2-}). The utilization of CBR is usually confined within the fields of animal feeding and anaerobic fermentation. CBR and CBR-chars have not been found to use for removing Cr(VI) from contaminated water until present.

The aim of this study was to investigate the specific chemical interactions between Cr(VI) and CBR (as well as CBR derived chars). Systematic tests were performed to investigate the effect of pyrolysis temperature on the surface and structural properties of prepared biochars, and to determine the roles of these properties in evaluating the performance of the biochars for capturing Cr(VI). The specific objectives were as follows: (1) establish a sustainable method to produce biochars from CBR, (2) compare the surface and chemical characteristics of biochars as influenced by temperature, (3) address the changes of CBR after carbonization that can impact the Cr(VI) capture behavior, and (4) clarify the possible removal mechanism of Cr(VI) by CBR and CBR chars.

Materials and methods

Sample preparation

Corn-bran residue (CBR) was collected from the Xiwang Group Co. Ltd. in Shandong, China, in which corn was deeply processed and produced starch. CBR sample was oven-dried at 80°C for 2 d, and then crushed by a high-speed universal crusher (FW-100, Tianjin Taisite Instrument Co. Ltd., China), whose sizes ranged from 60 to 120 mesh. The CBR powder was heated at the heating rate of 5°C min^{-1}, reaching the control temperatures of 300, 400, 500 and 600°C, respectively. Simultaneously, the pyrolysis process of CBR samples was kept under a nitrogen atmosphere for 2 h to obtain CBR-derived chars, which were labeled as CBR300, CBR400, CBR500, and CBR600, respectively. The samples were then placed into glass desiccators, cooling down to room temperature for 1.0 h, and stored in different sealed glass jars at ambient conditions for further use. Each sample was directly subjected to characterization without treatment.

Biochar characterization

The volatile matter and ash contents were determined by heating CBR and CBR-derived chars at 750°C for 4 h.[18] The sample pH was measured using an Orion 818 pH meter with a combination electrode after each sample was thoroughly mixed with deionized water at the mass ratio of 1:10, and then equilibrated for approximately 1 h. The point of zero charge (PZC) which is one of the most important parameters used to describe the variable charge surface of CBR and CBR-chars was determined by mass titration method. 0.1mol/L NaOH and 0.1mol/L HNO_3 were added into different concentrations of $NaNO_3$ solution (0.001, 0.01 and 0.1mol/L) to adjust the pH of the solution range from 1.0 to 11.0. After a certain amount of biochar was added into $NaNO_3$ solution, the suspensions were vibrated at 30°C and 150 rpm for 3 h. The pH of suspension was determined at steady state conditions, and then the quality of the titration curve was obtained by a mapping of pH and solid concentrations. With concentrations of solid increasing, the pH of suspensions tended to a stable value, which was known as the point of zero charge (pH_{PZC}). Besides, the C, N, O, and H contents of CBR and CBR-derived chars were detected by using a Heraeus Elemental Analyzer (Heraeus, Hanau, Germany). Specific surface area (SSA) was determined by using a Brunauer, Emmett and Teller (Quanta Chrome Chem BET-3000, USA) method of N_2 adsorption- desorption isotherms at 77.3 K. Fourier transform infrared (FT-IR) spectra were obtained by using FT-IR spectroscopy (IRPrestige-21, Schimadzu, Japan), covering the infrared region 4000-400 cm^{-1}.

Cr(VI) removal experiments

Potassium dichromate ($K_2Cr_2O_7$) was purchased from Sinopharm Chemical Reagent CO. (Shanghai, China). A Cr(VI) stock solution of 1000 mg/L was prepared by dissolving 2.829 g $K_2Cr_2O_7$ in 1000 ml deionized water. All the experimental solutions were subsequently prepared from this stock solution.

The Cr(VI) removal performance of the CBR and CBR-chars was evaluated at 30°C in a 250 ml Iodine flask. Generally, 5 g L^{-1} of one biochar was mixed with Cr(VI) solution in the flask. Then the mixture was shaken in a thermostatic shaker at 150 rpm for 8 h. Subsequently, the suspension was filtered with a 0.45 μm syringe filter, and the concentrations of Cr(VI) in the filtrate were measured by spectrophotometry at a wavelength of 540 nm using 1,5-diphenylcarbohydrazide (DPC) as the color reagent. To measure the total Cr concentration, Cr(III) was first converted to Cr(VI) at 130°C by adding excess potassium permanganate prior to reacting with DPC.[19] The amount of Cr(III) present was calculated from the difference between total Cr and Cr(VI).[20] The solution pH was adjusted by adding small quantities of concentrated H_2SO_4 or NaOH solution. The residual solids were water-washed and freeze-dried, subsequently stored in plastic bottles prior to further analyses. The removal efficiency (%) of Cr(VI) was calculated using Eq. (1)

$$\text{Removal efficiency (\%)} = \left(\frac{C_0 - C_t}{C_0}\right) * 100 \qquad (1)$$

where C0 and Ct (mg/L) represent the Cr(VI) concentrations at initial and final conditions, respectively.

The effects of initial Cr(VI) concentration on Cr(VI) removal by CBR and CBR-derived chars were investigated using the batch test. 200 ml Cr(VI) solution (50 mg L^{-1}) at pH 2,[21] was added into 1.0 g of one sample (5 g L^{-1}) in each of a series of 250-ml Iodine flasks. The initial Cr(VI) concentrations in the flasks were 50, 100,150, 200, 300, 400, and 500 mg L^{-1}, respectively. The samples for each Cr(VI) concentration were prepared in duplicate. Test conditions (e.g., temperature and rotation rate) and

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Cr analytic procedures were same as mentioned above. In addition, the effects of initial pH (1-6) and CBR-char amounts (0.5-6 g L^{-1}) on Cr(VI) removal were also evaluated at 50 mg L^{-1} of Cr(VI) and the pH of 2, and the optimal Cr(VI) removal efficiency was observed at 5 g L^{-1} of CBR-char.

Tests of each sample were conducted in triplicate and all results were the average of replicate analysis.

Results and discussion

Characterization of CBR and CBR-biochars

Elemental compositions of CBR and CBR-biochars were described in Table 1. Both elemental concentration of feedstock and pyrolysis temperature had strong influences on the elemental composition of biochars.[18, 22] The C content increased with increasing charring temperature, while H and O contents showed an opposite trend. The carbonization degree of biochars can be estimated using H/C atomic ratio because H is mainly associated with plant organic matter. As the charring temperature reached 300°C, the H/C ratio sharply decreased (H/C ratio of 0.819), indicating that the original organic fractions significantly decreased. CBR600 had the highest carbonization degree among all samples due to the lowest H/C ratio of 0.455, which was consistent with previous observations.[18] However, CBR had a high H/C ratio of 1.537 as well as a high content of sulfur oxide (SO_2, 320 mg/kg), suggesting that it has the potential as a reductant to convert Cr (VI) to less toxic Cr (III). When pyrolysis temperature reached 80°C, SO_2 was released from CBR, implying that the SO_2 contents of CBR-chars can be neglected. Furthermore, with increasing pyrolysis temperature, the O/C and/or (O+N)/C ratios decreased, suggesting a decrease of polar groups and an increase of hydrophobicity.[18]

Table 1 pH, pH_{PZC}, Ash contents, elemental compositions, atomic ratios, and SSA of the CBR and CBR-biochars produced at different pyrolysis temperatures.

pH, pH_{PZC}, ash, elemental composition, atomic ratio, surface area

Sample	pH	pH_{PZC}	Ash(%)	C (%)	H (%)	N (%)	O (%)	H/C	O/C	(O+N)/C	SSA(m^2/g)
CBR	4.02	3.89	6.12	44.12	5.65	4.24	45.99	1.537	0.782	0.864	0.447
CBR300	6.08	5.85	14.18	56.53	3.86	5.07	42.26	0.819	0.561	0.638	0.986
CBR400	6.89	6.63	20.07	65.68	3.70	5.11	25.51	0.676	0.292	0.358	1.420
CBR500	7.03	6.82	20.11	71.95	3.08	4.69	20.28	0.514	0.211	0.267	7.155
CBR600	8.92	8.74	21.43	73.36	2.78	4.47	19.39	0.455	0.198	0.250	58.232

The specific surface area (SSA) of CBR and CBR-chars plays a key role in determining the surface reactivity of these materials. The SSA of CBR was measured to be 0.447 m^2 g^{-1}, which was small. The reason was probably that N_2 molecules cannot access the internal surface of the lignocellulosic fibers of CBR.[7] The SSAs of CBR300, CBR400, and CBR500 were 0.986, 1.420 and 7.155 m^2 g-^{1}, respectively. The maximum SSA (58.232 m^2 g^{-1}) was achieved when the pyrolysis temperature was increased further to 600°C, indicating that new surface was created at the higher temperature. Consequently, CBR carbonization would result in a significant increase of CBR-char SSA, especially when the charring temperature was above 600°C.

The functional groups on the biochars can be associated with the surface characteristics of their parent feedstock. The FT-IR spectra are also in line with their elemental composition, and peaks exhibited at 1620, 1730, 2927 and 3269 cm^{-1} for the CBR (Fig.1). These peaks were assigned to the-COOH antisymmetric stretching of amino acids, straight chain C-C stretching (or sugar C-OH stretching), alkane -CH_2 symmetric stretching, and SO_3^{2-} stretching, respectively.[23] Increasing temperature could pose decreases of –CH_2, and an increase of C=C with the conversion from amphoteric (acid/basic) surface functional groups to aromatic ones.[24] The band intensity of the peak at 3400 cm^{-1} for CBR300 significantly declined, indicating that the dehydration of cellulosic component started at 300°C.[25] In addition, the SO_2 content decreased with increasing charring temperature, which resulted in the red-shifted in carboxyl group (C=O, 1706 cm^{-1}), and the disappearance of SO_3^{2-} peak (1038 cm^{-1}). Therefore, there was difference between CBR and CBR300 for the band 1706 and 1038 cm^{-1}. Some peaks in CBR-char weakened or disappeared when the charring temperature was increased to 400°C. This was the reasons that there were big spectral differences between (CBR, CBR300) and (CBR400, CBR500, CBR600).

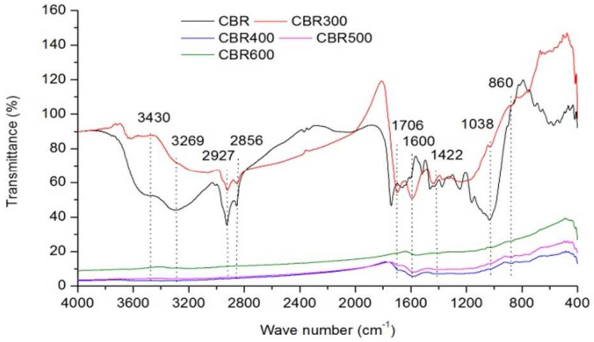

Fig.1. Functional groups present on CBR and CBR-chars inferred from FT-IR (cm^{-1})

The pH values for CBR and CBR-chars increased from 4.04 to 8.92 with increasing pyrolysis temperature (Table 1). This could be explained by four reasons as follows: (1) SO_2 released from CBR, resulting in the decrease of SO_2 contents in CBR-derived chars; (2) the peaks of 3269 and 1038 cm^{-1} (SO_3^{2-}) for the biochars disappeared when pyrolysis temperature increased (Fig.1); (3) during heating processes beyond 300°C, alkali salts leached from matrix structure, leading to pH rise;[26] (4) the peaks at 1422 and 1600 cm^{-1} occurred for both CBR and CBR300, and declined or disappeared for CBR600. Although the band intensity at 1730 cm^{-1} (ester C=O) was maximum for CBR, the intensity decreased and shifted to relatively low wave number of 1706 cm^{-1} with increasing pyrolysis temperature, where the functional groups were mainly occupied by carboxyl, and trace of esters, ketones and aldehydes.[25]

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Effect of initial pH on Cr(VI) removal

It was evident that the optimum efficiency of Cr(VI) removal largely relies on solution pH, Cr(VI) concentration, and adsorbent amounts.[7, 27] Solution pH influences Cr speciation and the dissociation of active functional groups (e.g., $-NH_2$, -OH, -COOH).[2] Besides, the adsorption reaction of Cr(VI) onto CBR or CBR-chars consumes large amounts of H^+ along with the reduction of Cr(VI) to Cr(III). The results of point of zero charge (PZC) tests indicated that quantity of functional groups such as SO_3-H and -COOH affected pH_{pzc} of CBR and CBR-chars (Table 1). With the quantity of acidic functional groups of these adsorbents decreased, their pH_{PZC} increased. At solution pH lower than pH_{PZC}, the total surface charge will be positive on average, where as at the higher solution pH it will be negative. The reductions of CBR and CBR-chars maybe play important roles when solution pH is lower than pH_{PZC}. Nevertheless, the adsorptions of these adsorbents are likely to be predominant when solution pH is higher than pH_{PZC}. Therefore, Cr removal is critically associated with solution pH. Cr(VI) removal by CBR and CBR-chars at 30°C and initial Cr(VI) concentration of 50 mg L^{-1} was found to be pH dependent as shown in Fig. 2. The Cr(VI) removal efficiencies of CBR and CBR400-600 were observed more than 95% at pH less than or equal to 2, suggesting that acidic pH range of 1-2 favored Cr(VI) removal process. This is because Cr(VI) is present in the form of either $[Cr_2O_7]^{2-}$ or $[HCrO_4]^-$ at lower pH and in the form of CrO_4^{2-} at pH higher than 5.5.[28] The surface of adsorbent could be protonated to a higher extent at a lower pH, and a strong attraction exists between these oxyanions of Cr (VI) and the positively charged surface of the adsorbent. Furthermore, a lower pH enhances the reducibility of some functional groups originating from CBR and derived chars, such as CxOH and SO_3^{2-}. Consequently, reduction and adsorption processes for Cr(VI) removal are further improved. These reductive reactions are described in Eqs. (2)-(4)

$$6C_xOH + Cr_2O_7^{2-} + 8H^+ = 6C_xO + 2Cr^{3+} + 7H_2O \qquad (2)$$

$$3C + 2Cr_2O_7^{2-} + 16H^+ = 3CO_2\uparrow + 4Cr^{3+} + 8H_2O \qquad (3)$$

$$Cr_2O_7^{2-} + SO_3^{2-} + 8H^+ = 2Cr^{3+} + SO_4^{2-} + 4H_2O \qquad (4)$$

Subsequently, Cr(III) adsorption was occurred at pH 5.0, where the number of negatively charged groups on the adsorbent increased and enhanced the Cr(III) removal by columbic attraction.[12]

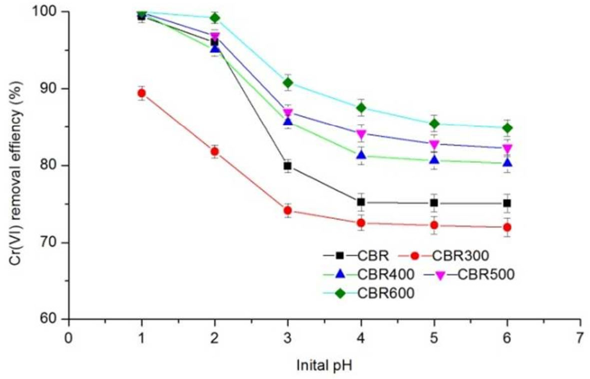

Fig.2. Effects of initial pH on Cr(VI) removal efficiency of CBR and CBR-derived chars at initial Cr(VI) concentration of 50 mg L^{-1}.

After CBR was mixed with the 50 mg L^{-1} Cr(VI) solution at pH 2, the Cr(VI) concentration decreased rapidly during 0.5 h (Fig.3). Since the rate of mass transferring from adsorbate to adsorbent was rapid enough, the removal reaction was rapid in initial stages. As reaction time increased, the Cr(III) concentration increased to 8.128 mg L^{-1} at 8 h, while the Cr(VI) concentration decreased to 1.99 mg L^{-1}, with the Cr(VI) removal reaching to 96.02%. This indicated that the removed Cr(VI) (9.60 mg g^{-1}) was partially converted to Cr(III) in solution, and the rest was bound to CBR (Fig. 2), which is similar to the enhanced removal of Cr(VI) by Na_2SO_3 combined with peanut straw biochar.[20] However, as solution pH increased, the Cr(VI) removal efficiency decreased significantly (Fig.2), with 96.02% obtained by CBR at pH 2, and 79.91% at pH 3. The low removal of Cr(VI) at pH 3 was likely due to the phenomenon of Cr(VI) reduction to Cr(III) for Cr sorption onto the CBR. As the solution pH rose from 3 to 6, the Cr(VI) removal efficiency continued to decrease. This was likely due to the increase competition from OH− for the sorption sites on the CBR and CBR-chars.[27] Furthermore, for the SO_3^{2-}-rich CBR, since SO_3^{2-} was sensitive to changes at the initial solution pH, the Cr(VI) could only be reduced by Na_2SO_3 within a narrow pH range of 2.0-2.4.[20]

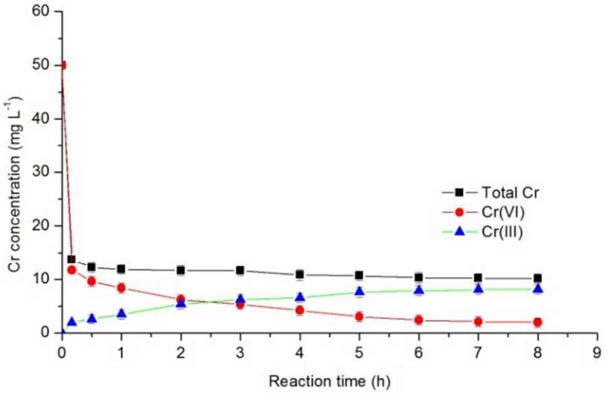

Fig.3 Effects of time on Cr concentration at initial pH of 2, and Cr(VI) concentration of 50 mg L^{-1}.

Cr(VI) adsorption and reduction also depended on both microporous structure and surface functionality. The carboxylic acid sites on CBR-chars could be appreciably deprotonated (COO−) at pH 2.0-3.2, which might bind some Cr(III).[29] Carboxyl groups on CBR-chars may have participated in Cr(III) adsorption process.[27] Moreover, the relative content of Cr(VI) bound to CBR-derived chars after Cr(VI) reaction with them, increased with the corresponding pyrolysis temperature.[7] The increase of pyrolysis temperature had a negative effect on the reduction capacity of the CBR-chars,[7] but higher temperatures could favor the improvement of their adsorption capacity for the derived chars. Consequently, the highest removal efficiency of Cr(VI) (99.21%) was obtained from CBR600 at pH 2, which was slightly higher than that of CBR (96.02%). However, Cr(VI) removal efficiencies of CBR and derived chars were all above 71.98% at pH range of 1-6, greater than that of activated carbon

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(63.28%) at pH 1.5 in previous study.[30] In addition, the materials had also better removal Cr(VI) capacity than those of rice bran and wheat bran, which were found to be less effective with the removal efficiency of only 50%.[31, 32] Cr(VI) removal capacity followed the sequence: CBR600 > CBR500 > CBR > CBR400 > CBR300 at pH of less than or equal to 2 (Figs. 2 and 3). On the other hand, the removal efficiency of Cr(VI) was demonstrated to increase with the increase of specific surface area (SSA), which increased with pyrolysis temperature, indicating that the pyrolysis biochars could really reduce and bind Cr(VI) for their removals. However, CBR is exactly more economical and effective for Cr (VI) removal compared with the derived chars, and has a promising application in the Cr (VI)-wastewater treatment.

Effect of initial concentration on Cr(VI) removal

The effects of initial Cr(VI) concentration on Cr(VI) removal by CBR and CBR-derived chars were investigated at initial pH 2 with adsorbent dose of 5 g L^{-1} (Fig. 4). As the initial Cr(VI) concentration increased from 50 to 500 mg L^{-1}, the amount of Cr(VI) removed by these added materials increased from 8.18 to 86.49 mg g^{-1}, while the removal efficiency decreased from 99.21 to 75.86%. The Cr(VI) concentration gradient between sorbate and adsorbent increased with increasing initial Cr(VI) concentrations, which contributed to improving the Cr(VI) adsorption capacity per unit weight of the adsorbent. The maximum removals of Cr(VI) were obtained 82.04, 75.86, 80.47, 83.98 and 86.49 mg g^{-1} for CBR, CBR300, CBR400, CBR500 and CBR600, respectively. It was found that the Cr(VI) removal capacities of coconut coir and derived chars ranged from 4.1 to 70.4 mg g^{-1},[7] which was similar to the current study. The Cr (VI) removal efficiencies of these materials were comparable to the reported one (99.4%) for rice bran.[33] As shown in Fig. 4, at the initial Cr(VI) concentrations of 50-150 mg L^{-1}, both CBR and CBR600 exhibited better Cr(VI) removal capacity than others. This may be attributable to the predominance of reduction and adsorption for CBR and CBR600 respectively.

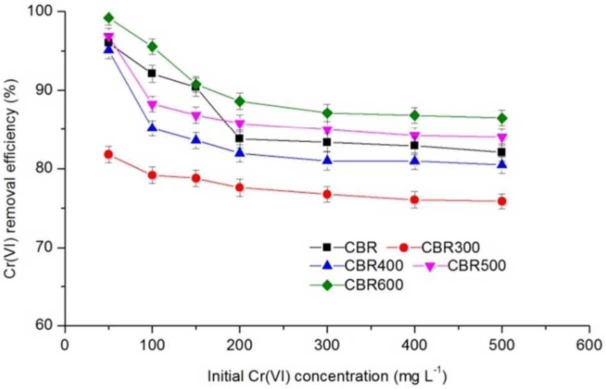

Fig.4. Effects of initial Cr(VI) concentration on Cr(VI) removals by CBR and CBR-derived chars at pH 2.

Freundlich equation was applied to fit the adsorption data obtained from the experiments using CBR and CBR-chars as adsorbents, as shown in Eq.(5).

$$q_e = K_F \cdot C_e^{\frac{1}{n}} \tag{5}$$

where Ce is the equilibrium concentration of Cr(VI) (mg L^{-1}) and qe is the amount of Cr(VI) adsorbed by per unit of CBR or CBR-chars (mg g^{-1}). K_F is associated with adsorption energy; while n represents the strength of the adsorption associated with characteristics of the adsorbent itself. Both K_F and n affect the adsorption isotherm, the larger the K_F and n values, the higher the adsorption capacity.[27]

On the other hand, the Langmuir model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer sorption without interaction between sorbed ions.[27] The model assumes uniform energies of sorption onto the surface and no transmigration of sorbate in the surface plane. It is described by Eq.(6).

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

where qm (mg/g) is the maximum quantity of metal ions per unit adsorbent to form a complete monolayer on the surface and b is a constant related to the affinity of binding sites with the metal ion.

The above parameters (K_F, n, q_m and b) were obtained by using Origin 8.0 software to fit the experimental data. The obtained parameters are shown in Table 2. With the exception of BCR300, the corresponding correlation coefficients (R^2) of Freundlich equation were above 0.98, indicating that Freundlich model can be used to describe the Cr(VI) adsorption behavior on the CBR and CBR-chars. The maximum adsorption capacities of CBR and CBR600 are similar because their n values are both around 1.45 (Table 2). Compared with the Freundlich model of Cr(VI) adsorbed by CBR and CBR-chars, the values of R^2 and qm of Langmuir model were around 0.50 and 42.83 mg L^{-1}, respectively, which indicated that Freundlich model provided better fit than Langmuir model. The results showed that the mechanism of Cr(VI) removal was complex and related with solution pH and materials characteristics. Therefore, CBR and CBR600 have similar removal capacities for Cr(VI) under acidic conditions, and both of them can be used as absorbents to remove Cr(VI) from acidic wastewaters.

Table 2 Parameters of Freundlich and Langmuir models for Cr(VI) removal.

Samples	Freundlich			Langmuir		
	K_F	n	R^2	q_e	b	R^2
CBR	3.89	1.43	0.99	40.99	4.32	0.546
CBR300	2.53	1.43	0.97	37.35	3.35	0.501
CBR400	1.70	1.19	0.99	39.75	4.04	0.504
CBR500	2.34	1.23	0.99	41.43	3.49	0.503
CBR600	4.52	1.45	0.98	42.83	3.58	0.506

Effect of biochar dosage on Cr(VI) removal

To determine the effect of adsorbent dosage, different amounts (0.5-6 mg L^{-1}) of adsorbent were suspended in 200 ml Cr(VI) solution, of which the Cr(VI) concentration was 50 mg L^{-1} and pH was 2, with contact time of 8 h. The amount of CBR and CBR-chars significantly affected the degree of Cr(VI) removal. As shown in Fig.5, the Cr(VI) removal efficiency increased with

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increasing the amount of adsorbent dosage, indicating that this can be attributed to the increase of surface area at a high dosage of the materials. By contrast, as adsorbent dosage increased from 0.5 to 6 g L^{-1}, the adsorption capacity decreased from 75.42 to 8.07 mg g^{-1} for CBR and from 83.56 to 9.99 mg g-1 for CBR600, respectively. The decrease of the Cr(VI) removal capacity was likely caused by the rising or dropping Cr(VI) concentration gradient between sorbate and adsorbent. The increasing adsorbent concentration may lead to a decrease of Cr(VI) amount adsorbed onto unit weight of adsorbent. The Cr(VI) removal degree was observed to be 75.42% and 83.56% for 0.5 g L^{-1} of CBR and CBR600, respectively. However, it obviously increased to 96.02% and 99.56% for CBR and CBR600 respectively when their concentrations were all 5 g L^{-1}. It was also found that slow changes in the Cr(VI) removal efficiencies occurred when the adsorbent dosage was over 5 g L^{-1}. At a higher adsorbent dosage (e.g., 6 g L^{-1}), the availability of high energy sites decreases, leading to a lower removal capacity for CBR (8.07 mg g^{-1}), and CBR600 (8.32 mg g-1), respectively. Therefore, 4-5 g L^{-1} of biochar addition level could be able to realize the adsorption-coupled reduction process and obtain a high-efficient removal of Cr(VI), which was similar to previous studies.[12, 20, 27]

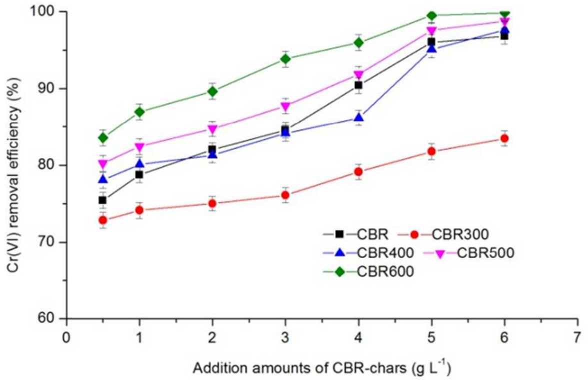

Fig.5. Effects of addition amounts of CBR or CBR-chars on Cr(VI) removal efficiency at initial pH 2 and Cr(VI) concentration 50 mg L^{-1}.

Mechanisms of Cr(VI) removal by CBR and CBR-chars

Characteristics of CBR and CBR-chars strongly depend on pyrolysis temperature, which in turn affects the Cr(VI) removal capacity of CBR and derived chars. The oxygen-containing functional groups on the surfaces of biochars determine the surface acidity-basicity and the adsorption properties of the materials.[7] It was hypothesized that CBR and CBR-chars effectively removed Cr(VI) through electrostatic attraction of Cr(VI) combined with Cr(VI) reduction to Cr(III) and Cr(III) complexation.[27] Furthermore, after adsorption, both Cr(VI) and Cr(III) were presented on the surface of CBR-chars produced at high temperatures, implying that a part of Cr(VI) was reduced during the adsorption process.[34]

Under strongly acidic conditions, the reduction of Cr(VI) by SO_3^{2-} migrated to Cr(VI) solution from the SO_3^{2-}-rich CBR played an important role (Fig.6). Compared with CBR before and after Cr (VI) adsorption, bands associated with SO_4^{2-} (1038 cm^{-1}) and $[Cr(OH)_4]^-$ (3430 cm^{-1}) increased due to the Cr(VI) oxidation (Fig.6). With the help of electrostatic driving forces, the negatively charged Cr(VI) speciation were captured by the positively charged surfaces of CBR or CBR-chars (protonated carboxylic, alcohol and hydroxyl groups) (Fig.1). Moreover, with the participation of H^+ and the electron donors from CBR or CBR-chars, Cr(VI) was reduced to Cr(III) under strongly acidic conditions (Fig. 3). Finally, a part of the converted Cr(III) was retained by the function groups on the materials, and the rest Cr(III) was released into the solution (Figs.3 and 6). Additionally, when solution pH was lower than pH_{PZC}, reduction by CBR and CBR-chars was predominant (e.g., CBR), while the adsorptions of these adsorbents played the leading roles in the Cr(VI) removal process under the condition of solution pH higher than adsorbent pH_{PZC} (e.g., CBR600). Therefore, the mechanism of Cr(VI) removal was complex, which included two processes of reduction and adsorption. When the accessible functional groups with Cr(VI) reduction capacity are ample with respect to the amount of Cr(VI) in the reaction system, Cr(VI) is completely reduced to Cr(III) after sufficient reaction time.[7] While the pure adsorption of Cr(VI) becomes relatively significant, such as CBR500 and CBR600.

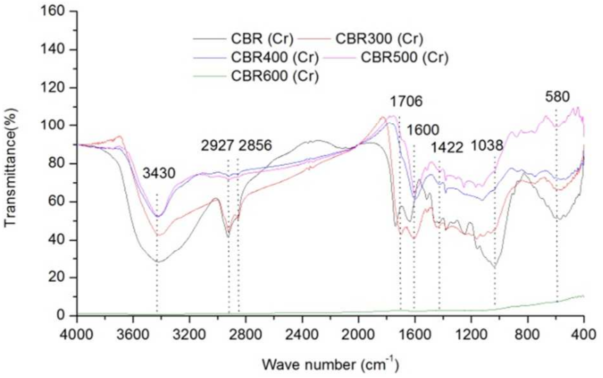

Fig.6. Functional groups present on CBR and CBR-chars inferred from FT-IR (cm^{-1}) after Cr adsorption under the conditions of initial pH of 2, Cr(VI) concentration of 50 mg L^{-1}, and adsorbent dosage of 5 g L^{-1}.

Conclusions

Compared with CBR-chars produced at lower temperatures, those produced at higher temperatures have large SSAs and lower contents of functional groups. The Cr(VI) removal efficiencies of CBR and CBR400-600 were more than 95% at low pH (1-2) , showing that strong acidity favored the Cr(VI) removal process. As the pH of aqueous was 2, the amount of Cr(VI) removed by the materials ranged from 8.18 to 86.49 mg g^{-1} at initial Cr(VI) concentrations of 50-500 mg L^{-1}. The Cr(VI) adsorption behaviors onto CBR and CBR-chars followed the isothermal model of Freundlich at solution pH 2. The mechanism of Cr(VI) removal by CBR and CBR-derived chars is the reduction coupled with adsorption of Cr(VI). Furthermore, CBR is demonstrated to be more economical and effective for Cr (VI) removal than the others.

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Graphical Abstract

Biochars were prepared from corn-bran residue (CBR) in low pyrolysis at temperatures range from 300 to 600°C. The CBR and CBR-derived chars were characterized and utilized to removal Cr(VI) from aqueous solutions. Temperature had strong influence on the elemental composition and surface characteristics of CBR-chars. Although CBR was comparable to CBR600 produced at 600°C in terms of Cr(VI) removal capacity, the mechanisms of Cr(VI) removal were different. For the SO_3^{2-}-rich CBR, the Cr(VI) removal mainly contributed to some reducing groups (e.g., SO_3^{2}, C-OH, -OH). However, the Cr(VI) removal capacity of CBR600 was attributed to adsorption predominance.

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Table and Figure Captions

Tables

Table 1 pH, Ash contents, elemental compositions, atomic ratios, and SSA of the CBR and CBR-biochars produced at different pyrolysis temperatures.

Table 2 Parameters of Freundlich and Langmuir models for Cr(VI) removal.

Table 1

pH, ash, elemental composition, atomic ratio, surface area										
Sample	pH	pH_{PZC}	Ash(%)	C (%)	H (%)	N (%)	O (%)	H/C	O/C	(O+N)/C	SSA(m^2/g)
CBR	4.02	3.89	6.12	44.12	5.65	4.24	45.99	1.537	0.782	0.864	0.447
CBR300	6.08	5.85	14.18	56.53	3.86	5.07	42.26	0.819	0.561	0.638	0.986
CBR400	6.89	6.63	20.07	65.68	3.70	5.11	25.51	0.676	0.292	0.358	1.420
CBR500	7.03	6.82	20.11	71.95	3.08	4.69	20.28	0.514	0.211	0.267	7.155
CBR600	8.92	8.74	21.43	73.36	2.78	4.47	19.39	0.455	0.198	0.250	58.232

Table 2

Samples	Freundlich			Langmuir		
	K_F	n	R^2	q_e	b	R^2
CBR	3.89	1.43	0.99	40.99	4.32	0.546
CBR300	2.53	1.43	0.97	37.35	3.35	0.501
CBR400	1.70	1.19	0.99	39.75	4.04	0.504
CBR500	2.34	1.23	0.99	41.43	3.49	0.503
CBR600	4.52	1.45	0.98	42.83	3.58	0.506

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Figures

Fig.1. Functional groups present on CBR and CBR-chars inferred from FT-IR (cm^{-1}).

Fig.2. Effects of initial pH on Cr(VI) removal efficiency of CBR and CBR-derived chars at initial Cr(VI) concentration of 50 mg L^{-1}.

Fig.3 Effects of time on Cr concentration at initial pH of 2, and Cr(VI) concentration of 50 mg L^{-1}

Fig.4. Effects of initial Cr(VI) concentration on Cr(VI) removals by CBR and CBR-derived chars at pH 2.

Fig.5. Effects of addition amounts of CBR or CBR-chars on Cr(VI) removal efficiency at initial pH 2 and Cr(VI) concentration 50 mg L^{-1}.

Fig.6. Functional groups present on CBR and CBR-chars inferred from FT-IR (cm^{-1}) after Cr adsorption under the conditions of initial pH of 2, Cr(VI) concentration of 50 mg L^{-1}, and adsorbent dosage of 5 g L^{-1}.

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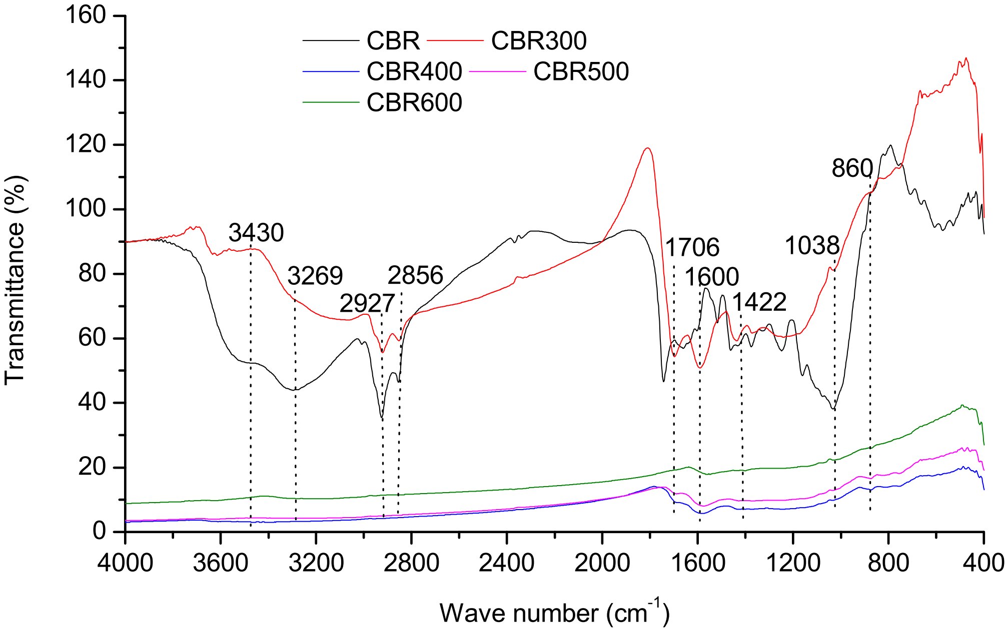

Fig.1

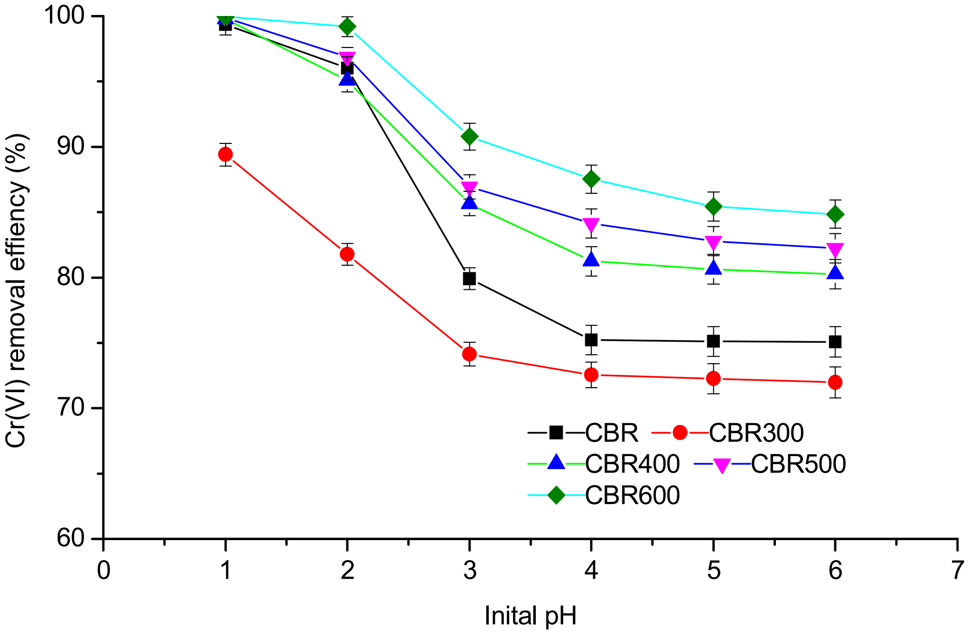

Fig.2

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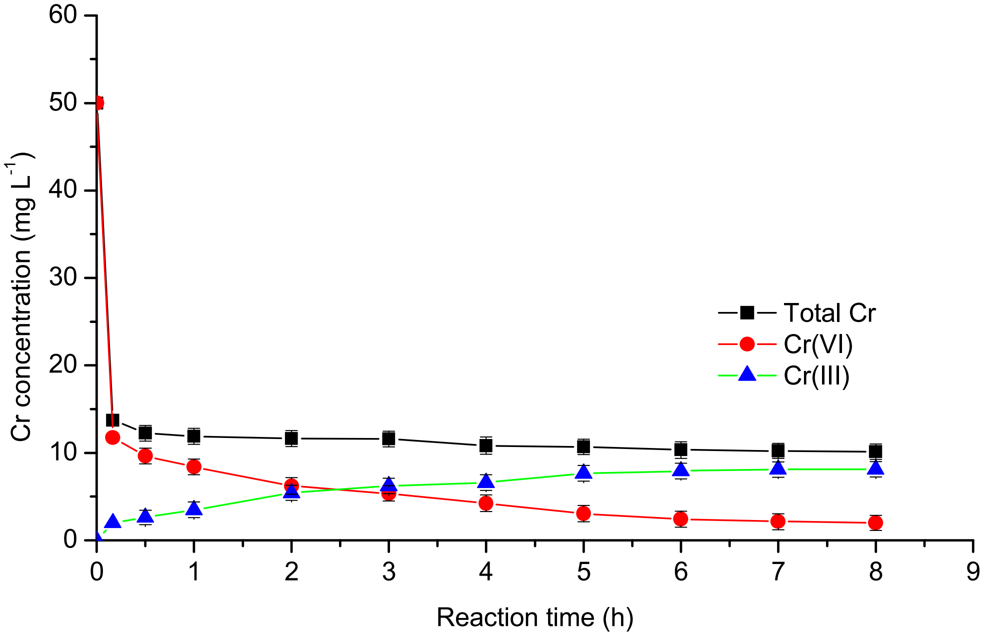

Fig.3

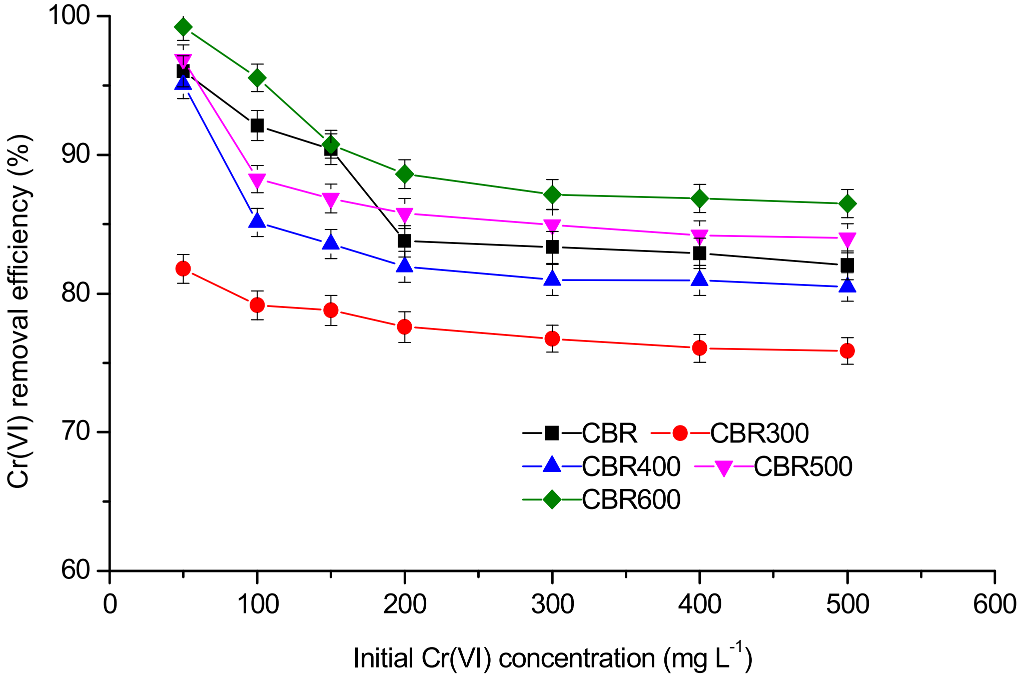

Fig.4

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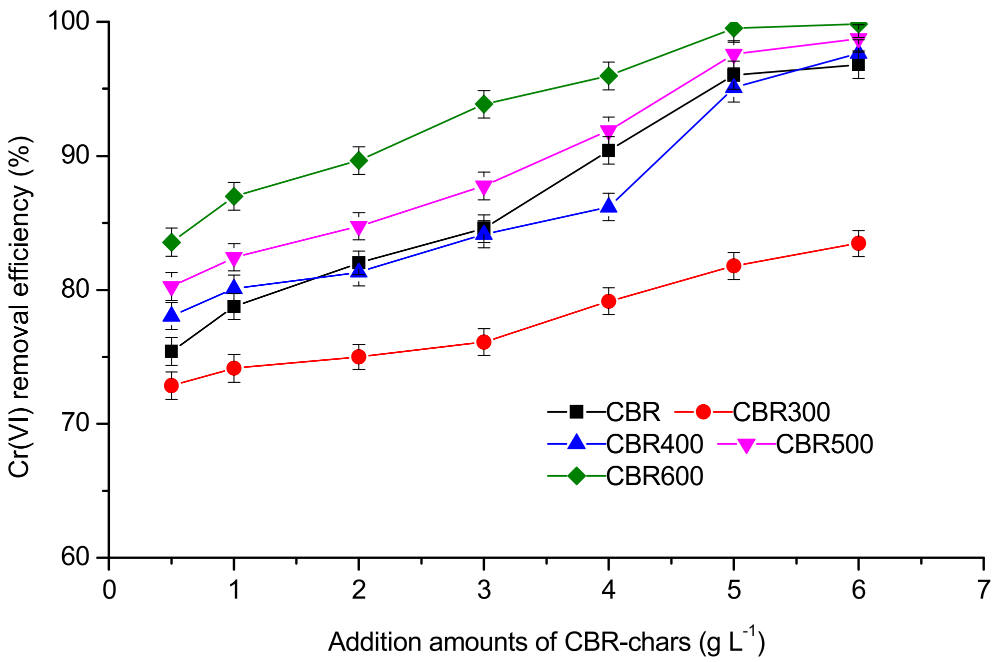

Fig.5

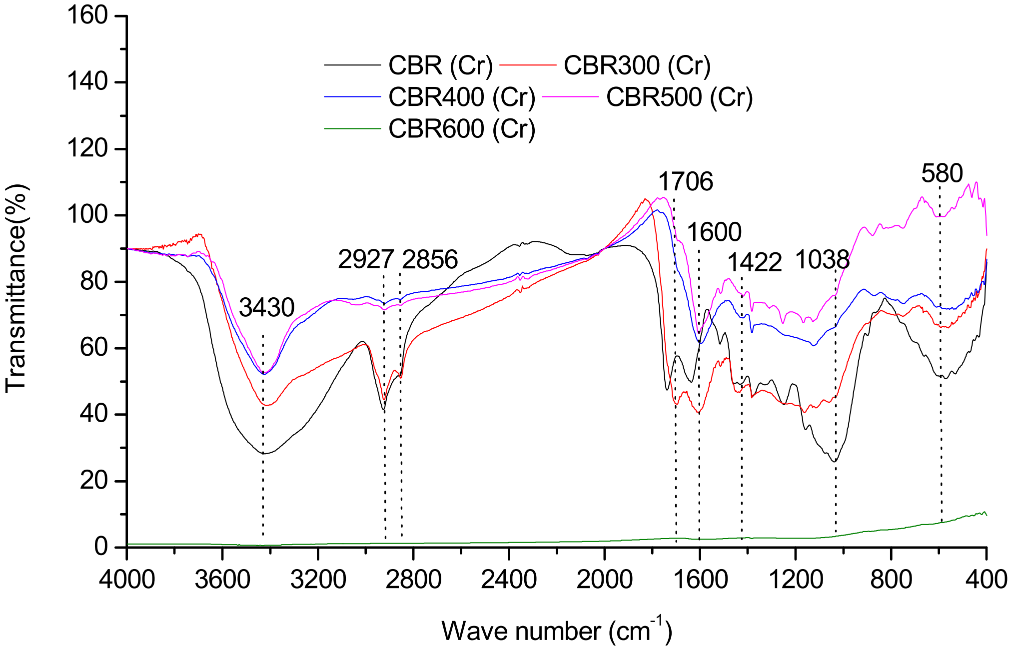

Fig.6

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