



Particles from bird feather: A novel application of an ionic liquid and waste resource

Ping Sun^b, Zhao-Tie Liu^{a,b,*}, Zhong-Wen Liu^{a,b}

^a Key Laboratory of Applied Surface and Colloid Chemistry (Shaanxi Normal University), Ministry of Education, Xi'an 710062, PR China

^b School of Chemistry & Materials Science, Shaanxi Normal University, Xi'an 710062, PR China

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ABSTRACT

The dissolution and regeneration of the waste chicken feathers in an ionic liquid of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) were demonstrated for preparing chicken feather based particles. The structure and properties of the regenerated chicken feathers were investigated by FT-IR, XRD, SEM, BET and water contact angle. The crystallinity of the regenerated chicken feathers was decreased, and the content of β -sheet was 31.71%, which was clearly lower than the raw feather (47.19%). The surface property of chicken feather changed from hydrophobicity to hydrophilicity after regenerated from [BMIM]Cl as indicated by the change of the water contact angle from 138 to 76°. The chicken feather particles regenerated from [BMIM]Cl showed an excellent efficiency (63.5–87.7%) for removing Cr(VI) ions in wastewater at the concentrations from 2 to 80 ppm. The Freundlich constant (k_F) for the adsorption of Cr(VI) ion by the particles of the regenerated chicken feather was four times larger than that of the raw chicken feather, the possible reason is the hydrophilic groups such as amino and carboxyl groups were tend to self-assemble towards surface when the dissolved CF were regenerated by water, amino group will partly hydrate to cationic amino and Cr(VI) ion occurs as an anion in the aqueous phase, so the cationic amino will adsorb the anionic Cr(VI) ion onto the RCF particles through electrostatic attraction. This work demonstrated a new application of the ionic liquid for dissolving chicken feather and a renewable application of waste chicken feather for removing Cr(VI) ion in water.

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1. Introduction

Bird feathers are composed mainly of keratins, i.e., a kind of self-organized protein. Thus, the feathers are very important sources of natural organic compounds and amino acids in the world. However, a great majority of the feathers, especially chicken feathers (CF), are still treated as a waste product currently, and only a small portion is utilized because the procedure for the utilization of feather is difficult [1]. Feathers are rich in protein, but the digestibility of the protein is very low. Alternatively, much work has been focused on the hydrolysis of feathers to obtain high value-added products [2]. However, the hydrolysis is commonly proceeded in superheated water (up to be of 220 °C and 22 bar), leading to the decomposition of some amino acids such as cystine and cysteine. CF can be used to remove heavy metals from waste water, such as Zn²⁺, Cu²⁺, Ni²⁺ [3–5], and selective As(III) adsorption [6]. Dyes also can be adsorbed by CF [7–10].

Compared to the limited number of molecular solvents available today, ionic liquids have attracted great attentions as green solvents with many combinations that offer an unprecedented versatility and tenability. Ionic liquids have been used successfully to dissolve several biological macromolecules such as starch [11,12], cellulose [13,14], and protein [15]. Swatloski et al. found that up to be of 25% (w/w) cellulose can be dissolved into the ionic liquid of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) [13]. Phillips et al. reported that the ionic liquid [BMIM]Cl can be used to prepare solutions of up to be of 13.2% (w/w) silk fibroin, and a 9.5% (w/w) silk in [BMIM]Cl solution at 100 °C was used to cast films on both silicon wafers and glass slides [15]. [BMIM]Cl has also been developed for the dissolution and regeneration of wool fibers [16].

[BMIM]Cl is effective for disrupting hydrogen bonding in different materials [11–16], and is reasonably expected to be an attractive solvent for bird feathers. In this study, [BMIM]Cl was synthesized and applied to dissolve and regenerate to prepare particles from feathers, and the properties of feather particles were evaluated. The solution of ionic liquid and feathers can be regenerated to form particles. The property of chicken feather changed from hydrophobicity to hydrophilicity after regenerated from the dissolution of ionic liquid. The regenerated particles showed an excellent

* Corresponding author at: Key Laboratory of Applied Surface and Colloid Chemistry (Shaanxi Normal University), Ministry of Education, Chang'an South Road #199, Xi'an 710062, PR China. Tel.: +86 29 85303682; fax: +86 29 85307774.

E-mail address: ztliu@snnu.edu.cn (Z.-T. Liu).

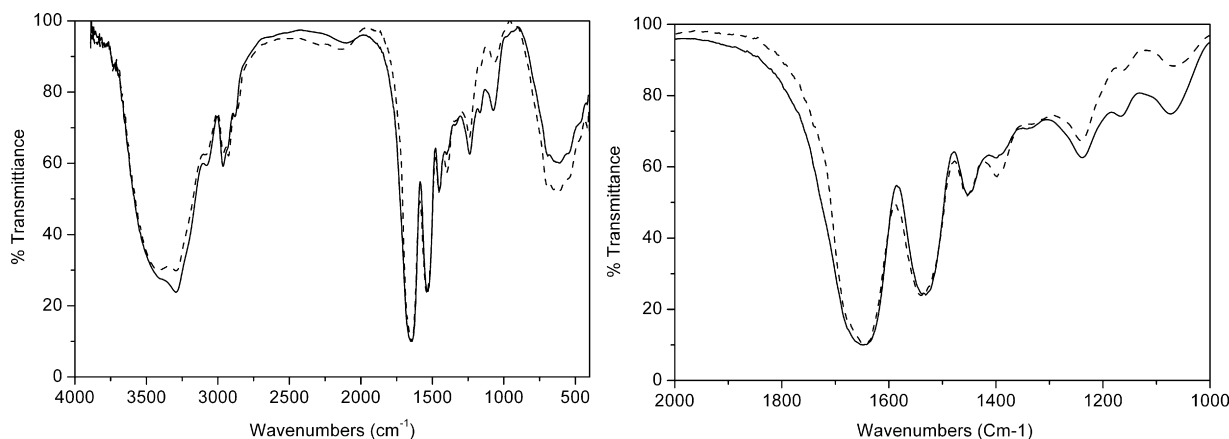


Fig. 1. IR spectra of CF (---) and RCF particles (-).

adsorbent for removing Cr(VI) ion in water under a very low concentrations from 10 to 80 ppm.

2. Experimental

n-Butyl chloride (CP grade) was distilled over CaCl_2 under inert gas atmosphere, and *N*-methylimidazole was freshly distilled from potassium hydroxide.

CF originated from slaughtered cock were immersed into 3% (w/v) sodium dodecylbenzene sulfonate solution for 1 h, and this step was carried out for three times. After filtering, the pretreated feathers were washed thoroughly with distilled water. The dissolution experiments were conducted under an inert atmosphere of Ar.

[BMIM]Cl was prepared by a modified method reported in literature, [17] and characterized by FT-IR and ^1H NMR. ^1H NMR (300 MHz, CDCl_3 , δ /ppm relative to TMS) δ : 0.80 (t, 3H, 3JHH = 7.3), 1.23 (m, 2H), 1.75 (m, 2H), 3.98 (s, 3H), 4.19 (t, 2H, 3JHH = 7.4), 7.46 (s, 1H), 7.63 (s, 1H), 9.55 (s, 1H).

IR spectra were recorded on Nicolet 870 using KBr pellets. X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/max-3c apparatus with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154$ nm). Scanning electron microscopy (SEM) images were obtained on a Philips-FEI Model Quanta 200. The specific surface area of powder was measured via nitrogen adsorption using Brunauer–Emmett–Teller (BET) surface area analysis on the ASAP 2020M. The concentrations of Cr(VI) were analyzed on TAS 986 atomic absorption spectrophotometer. The degree of hydrophobicity of samples was measured using a DCAT 21 contact angle meter.

The dissolution experiments were conducted under an inert atmosphere of N_2 due to the hygroscopic nature of the [BMIM]Cl. The temperatures of the ionic liquid solutions were maintained with a temperature-controlled oil bath at 100°C . The solubility of CF by weight can be up to be of 23% including rachis after stirring for 48 h, and a brownish transparent viscous solution was obtained. The feather particles can be regenerated from the solution obtained by adding ethanol, or water. The solution was suspended in water under vigorous stirring for 30 min, then filtered, and washed with ethanol several times to remove water, followed washed with ether to remove ethanol, and grayish-white particles were obtained. To decrease the agglomeration of particles, keep the water or ethanol level above the layer of the precipitation when filtrating.

Chromium ions solutions in the range of 2–80 ppm were prepared from potassium bichromate. Batch sorption tests were conducted by placing 0.125 g of the above-mentioned adsorbents in bottles containing 25 ml of an aqueous solution of Cr(VI) ions of a predetermined concentration. The suspension was agitated in a

shaker and samples were allowed to reach equilibrium (24 h) and then filtered. The residual Cr(VI) ion contents in the filtrate were analyzed using an atomic absorption spectrophotometer. A blank experiment was conducted in the absence of sorbent and no metal sorption by the bottle or by the filter paper employed was detected.

3. Results and discussion

3.1. FT-IR and the structure of regenerated CF particles

Infrared absorption spectra of CF and RCF (Fig. 1) show characteristic absorption bands assigned mainly to the peptide bonds ($-\text{CONH}-$). The vibrations in the peptide bonds originate bands known as amides I–III [18]. The amide I band is connected mainly with the $\text{C}=\text{O}$ stretching vibration and it occurs in the range of $1700\text{--}1600\text{ cm}^{-1}$. The amide I of CF peaks at 1641 cm^{-1} , and RCF at 1646 cm^{-1} . The amide I peak of RCF shifted to higher wavenumber was an indicative of more disordering structure. The amide II is related to N-H bending and C-H stretching vibration. The amide II of CF peak is at 1531 cm^{-1} , and RCF is at 1529 cm^{-1} . The amide III band occurs in the range of $1220\text{--}1300\text{ cm}^{-1}$ and it results from in phase combination of C-N stretching and in N-H in plane bending, with some contribution from C-C stretching and C=O bending vibrations. The amide III of CF peaks at 1240 cm^{-1} , and RCF is at 1239 cm^{-1} . Finally the intense peaks at 1167 and 1073 cm^{-1} are related, respectively, to the asymmetric and symmetric S-O stretching vibrations of the bunte salts residues [19]. For RCF, the absorption intensity increased compared with that of CF indicated that S-S bonds have been destroyed.

FT-IR analysis can be used to assess secondary structure in proteins. Amide I originated from C=O stretching vibrations and has been shown a sensitive indicator of different types of protein secondary structure [20]. Table 1 summarizes results of the deconvolution of the amide I band into individual components representing various structural conformations. Peaks were assigned according to Goormaghtigh et al. [20]. For RCF, the ratio of α -helix and β -sheet (ordered) decreased, while the ratio of random and β -turn increased in compared with CF. Yu et al. suggested that the difference in percentage of protein secondary structure may be partly responsible for different feed protein digestive behaviors [21]. The

Table 1
Summary of FT-IR amide I deconvolution.

Sample	α -Helix (%)	β -Sheet (%)	β -Turn (%)	Random (%)
CF	9.38	47.19	32.25	11.18
RCF	5.26	31.71	47.48	15.55

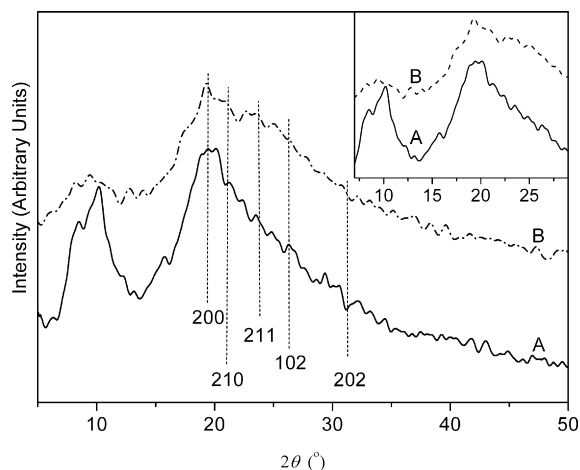


Fig. 2. XRD analysis for Feather (A), and RCF (B).

low digestibility of feather protein is related to several structural characteristics such as the high keratin content, the strong disulfide bonding of the amino acids, and the relationship of β -sheet to solubility. The decrease in β -sheet structure of RCF may result in increase in digestibility.

3.2. XRD

The crystal structures of RCF and the raw feather were analyzed by XRD as shown in Fig. 2. The diffraction peak at 2θ of about 9.8° corresponding to the α -helix structure, and the peaks at 2θ of 19.5° and 21.2° , indexed as the β -sheet crystalline structure were clearly observed for the raw feather (Fig. 2A) [16]. In the case of the regenerated feather (RCF) (Fig. 2B), the intensity decreased remarkably, indicating that the crystallinity of RCF decreased. The diffraction peak corresponding to the intensity of α -helix structure decreased obviously, indicating that the α -helix structure of amino acid is difficult to be reserved in the regenerated feathers. Moreover, a very broad peak centered at 2θ of about 25.0° (Fig. 2B) was appeared for the RCF, which may be due to the overlapping of the β -sheet and β -turn peaks. These results are consistent with that of the FT-IR.

3.3. SEM

Fig. 3 shows the SEM images of CF and RCF. Feather's side branches have even finer sub-branches in contour feathers. The side

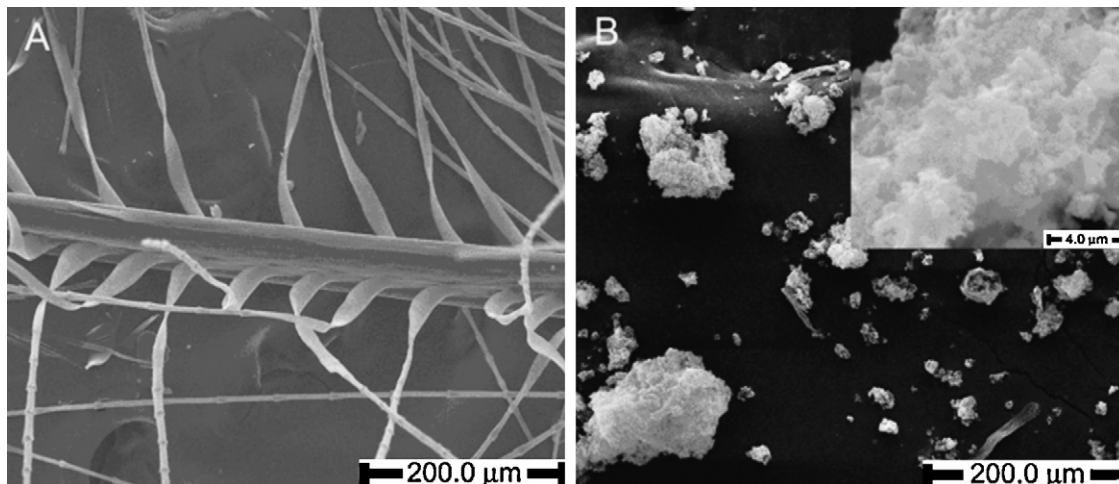


Fig. 3. SEM images of CF (A) and RCF (B).

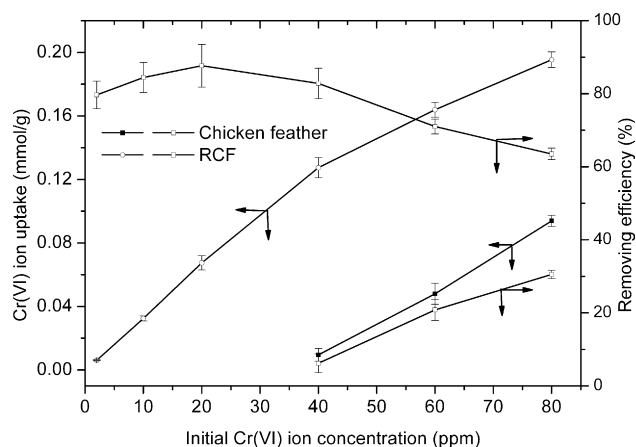


Fig. 4. Effect of Cr(VI) ion concentrations on uptake by chicken feather and RCF.

branches in these are called barbs and are linked together by a set of barbules. Barbs have side branches of their own called barbules [22]. In the case of RCF, there are not any barbs or barbules, just some particles accumulated to each other, indicating that CF was dissolved in [BMIM]Cl successfully.

3.4. Sorption of Cr(VI) ions by CF and RCF

Cr(VI) is acutely toxic, and occurs as HCrO_4^- , CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$ anions in water [23]. Many biomasses were used as biosorption of Cr(VI) ions from water [24–29], most of them show high sorption capacity at low pH values, because the surface charge of sorbents should be positive at low pH, and this should promote the binding of the negatively charged Cr(VI) ions. CF is composite of keratin [1], abound of amine groups exist in CF, and amine groups can easily form cationic ions, and this should promote the binding of the negatively charged Cr(VI) ions in relatively mild condition. So the sorption behaviors of Cr(VI) by CF and RCF were investigated.

The amounts of Cr(VI) ions removed by the CF and RCF were determined by varying the initial Cr(VI) ion concentrations in the presence of fixed amounts of adsorbent (Fig. 4). Thus, the initial metal ion concentrations were varied in the ranges of 2–80 ppm, and initial pH values were in the ranges of 5.30–4.08. For CF, no sorption was found when the initial metal ion concentrations are lower than 40 ppm. However, when it is higher than 40 ppm, an increase in the initial metal ion concentrations leads to an increase

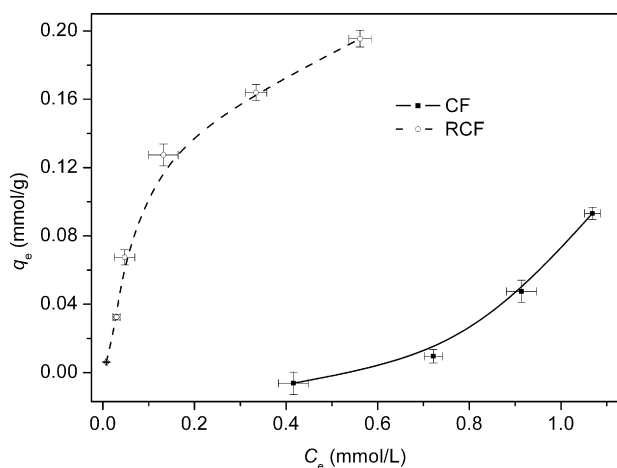


Fig. 5. Adsorption isotherms for sorption of Cr(VI) ion by CF (■) and RCF (○).

in uptake, the removing efficiency ranges from 6.2 to 30.5%, indicating that that CF is not an ideal adsorbent for adsorbing Cr(VI) ions. Excitedly, we found that the RCF exhibited a preeminent performance of adsorbing Cr(VI) ions, the removing efficiency ranges from 63.5 to 87.7%. Most of Cr(VI) ions were adsorbed by RCF, even at the initial metal ion concentration of 2 ppm. After adsorbed by RCF, the final pH values of Cr(VI) aqueous solutions were nearly neutral.

Fig. 5 shows adsorption isotherms for sorption of Cr(VI) ion by CF and RCF. For CF, the adsorption isotherm may attribute to S type (type) [30]. At pH 3–5, tetrahedral chromate ions, CrO_4^{2-} ions present as dominant species [23], the S type adsorption isotherms indicated that Cr(VI) ions have moderate intermolecular attraction with CF surface, causing them to pack vertically in a regular array in the adsorbed layer; and Cr(VI) ions meet strong competition, for substrate sites, from molecules of the solvent [30], in practice, negative value is obtained at low concentrations of Cr(VI) ion. While for RCF, the adsorption isotherm is L type, the slope of isotherm is very large at initial process; the curvature shows that as more sites in the substrate are filled it becomes increasingly difficult for a bombarding solute molecule to find a vacant site available. It suggested that there is no strong competition from the solvent.

The equilibrium isotherms for the sorption of Cr(VI) ion over CF and RCF are presented in Fig. 6 in terms of the linearized Freundlich

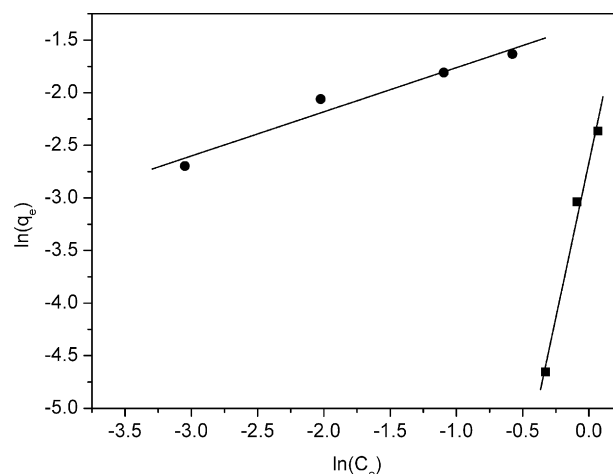


Fig. 6. Freundlich isotherms for sorption of Cr(VI) ion by CF (■) and RCF (●).

Table 2

Freundlich constants for sorption of Cr(VI) ion by chicken feather and RCF.

Sorbent	k_F	n	R
CF	0.0698	0.1694	0.9931
RCF	0.3106	1.7741	0.9803

isotherm:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (1)$$

where C_e (mmol L^{-1}) is the sorbate concentration in the solution, and q_e (mmol g^{-1}) is that adsorbed by sorbent at equilibrium. k_F and n are the Freundlich coefficients. The value of k_F is related to the adsorption capacity while the value of n is related to the adsorption intensity. The linearized Freundlich isotherm model fits the equilibrium experimental data quite well for CF and RCF for removing Cr(VI) ion (Fig. 6). It is seen that the sorption capacity of RCF is much higher than that of CF.

The Freundlich constants for both CF and RCF are presented in Table 2. From the values of k_F , it can be concluded that the sorption capacity of RCF is four times larger than that of the raw CF. The value of n is related to the adsorption intensity, n is usually greater than 1, however, for CF, the n is quite lower than 1, suggesting that the adsorption intensity between CF and Cr(VI) ion is very weak, while for RCF, the n is 1.7741, which is much greater than that of CF,

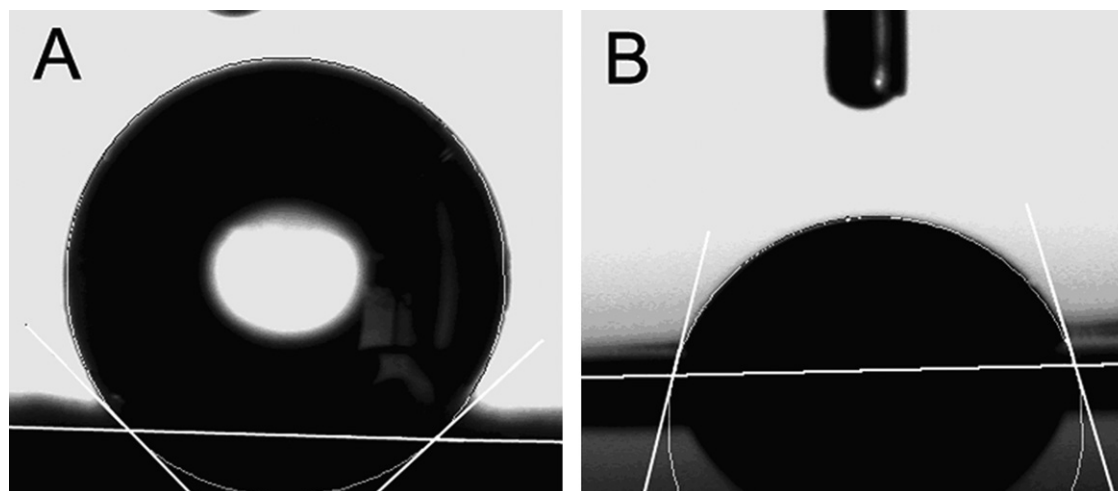


Fig. 7. Photomicrographs of water contact angle. (A) CF (138°); (B) RCF (76°).

indicating that the adsorption intensity between RCF and Cr(VI) ion is much greater than that of CF.

The sorption capacity of materials is mainly affected by two facts, specific surface area and the character of surface. To investigate the possible reason of improving in removing of Cr(VI) ion by RCF, the specific surface areas of chicken feather and RCF were analyzed by Brunauer, Emmett and Teller (BET) adsorption–desorption of nitrogen gas. It is surprised that the specific surface area of CF ($654 \text{ m}^2 \text{ g}^{-1}$) is larger than that of RCF ($493 \text{ m}^2 \text{ g}^{-1}$). So the main fact that affected the sorption capacity of CF and RCF is not the specific surface area, but the property of surface.

3.5. Water contact angle

Surface properties of CF and RCF were measured via water contact angle, and the images are shown in Fig. 7. The results indicate that CF is a kind of strong hydrophobic material (water contact angle of 138°), so CF may act as hydrophobic materials, such as crude oil and lipin. However, the water contact angle of RCF is 76° , which shows hydrophilicity. It is helpful for us to understand why the sorption capacity towards Cr(VI) ion by RCF increased four times. The hydrophilic surface is compatible with the hydrophilic Cr(VI) ion, so the uptake increased greatly as compared with that of CF. However, the reasons why the surface of RCF changed from the hydrophobic surface of CF to the hydrophilic one are complicated. A possible reason is that the secondary structures of CF were changed in dissolving process, and when regenerated by water, the hydrophilic groups such as amino and carboxyl groups were tend to self-assemble towards water phase, so the surface of RCF changed to hydrophilicity. Meanwhile, the pH of water normally is about 6, and in this condition, amino will partly hydrate to cationic amino and Cr(VI) ion occurs as an anion in the aqueous phase, so the cationic amino will adsorb the anionic Cr(VI) ion onto the RCF particles through electrostatic attraction.

4. Conclusions

[BMIM]Cl shows strong ability to dissolve CF by effectively disrupting the hydrogen bonds in the feathers. The solution of ionic liquid and feathers can be regenerated to form feather particles. The regenerated feathers decrease in β -sheet content remarkably, and perform hydrophilicity. The regenerated CF particle showed an excellent efficiency (63.5–87.7%) for removing Cr(VI) ions in waste water at the concentrations from 2 to 80 ppm. The Freundlich constant (k_F) for the adsorption of Cr(VI) ion by the particles of the regenerated chicken feather was four times larger than that of the raw chicken feather.

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