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γ-ray radiation-induced synthesis and Fe(III) ion adsorption of carboxymethylated chitosan hydrogels

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ABSTRACT

The carboxymethylated chitosan (CMCts) hydrogels were synthesized by γ-ray radiation-induced crosslinking at paste-like state with the concentration of CMCts from 12% to 22%. The gel fraction firstly increased with adsorbed dose and leveled off at ca. 20 kGy. The diffusion behavior of water in CMCts gels was Fickian diffusion, and the swelling of CMCts gels was affected by pH and ionic strength. Preliminary crosslinking mechanism of CMCts with γ-ray irradiation was discussed based on the FTIR and sol-gel analysis. The adsorption kinetics study showed that the adsorption of Fe(III) ions onto CMCts gels was very fast (ca. 20 min) due to the coordination of Fe(III) ions with amino, hydroxyl and carboxyl groups of CMCts molecules. pH 4.7 was the optimum for the adsorption of Fe(III) ions onto CMCts gels. The maximum uptake of Fe(III) ions, based on Langmuir equation, was determined to be 18.5 mg/g gel.

1. Introduction

In the past few decades, a great interest has been focused on a naturally occurring class of polymers called polysaccharides for their large amount in nature, biodegradability and extensive applications. For example, chitin/chitosan are a species of abundant polysaccharides and have been used as suitable natural polymers for the adsorption and separation of metal ions because the amino and hydroxyl groups on the chitin/chitosan molecular chains can act as coordination sites for metal ions (Burke, Yilmaz, Hasirci, & Yilmaz, 2002; Chu, 2002; Guibal, 2004; Kumar, 2000; Park, Park, & Woo, 1999). Furthermore, by substituting carboxymethyl groups for some hydrogens of the hydroxyl or amino groups of chitosan molecules, carboxymethylated chitosan (CMCts) is prepared, which offers more coordination groups, i.e. carboxyl groups, to increase adsorption capacity toward some metal ions (Hon & Tang, 2000; Sun & Wang, 2006). The application of CMCts can be wider in the form of hydrogels due to its ability to maintain large amount of the solvent and substance.

Radiation crosslinking has been proved to be a safe, clean and effective method for hydrogel synthesis. Compared with conventional chemical routines, neither initiator nor crosslinker is needed in most of the cases when using radiation methods so that the products are free of toxicity additives. Yoshii and his coworkers (Wasikiewicz, Nagasawa, Tamada, Mitomo, & Yoshii, 2005; Zhao, Mitomo, Nagasawa, Yoshii, & Kume, 2003; Zhao, Wasikiewicz, Mitomo, Nagasawa, & Yoshii, 2007; Zhao et al., 2008) have synthesized the hydrogels based on carboxymethylated chitin derivatives by electron beam (EB) irradiation and investigated their applications for adsorption of some metal ions (e.g. Au ions) and humic acid. They found firstly that carboxymethylated chitin derivatives could be crosslinked and used as good adsorbents. However, the radiation-induced crosslinking mechanism of CMCts, as well as the diffusion behavior of water in CMCts gels, etc., has not been investigated in detail, which is very important for its further applications in adsorption and separation. In our previous work, radiation crosslinked hydrogels, such as polydimethylaminaethyl methacrylate (PDMAEMA) hydrogels has been investigated for adsorption of metal ions (Yan et al., 2004). Moreover, γ-ray radiation-induced change of CMCts in solid state and dilute aqueous solution under the irradiation of ^{60}Co source have also been investigated in detail (Huang, Peng, Zhai, Li, & Wei, 2007a; Huang, Zhai, Peng, Li, & Wei, 2007b). In this work, we would report γ-ray radiation-induced crosslinking of CMCts, the diffusion behavior of water in CMCts gels as well as its novel application for the adsorption of Fe(III) ions.

Iron is the fourth most abundant element in the earth's crust, and is very important in the biosphere (Ngah, Ab Ghani, & Kamari, 2005). Waste effluents from steel tempering, coal coking, mining industries and so on, contain large quantities of iron (Aksu, Calik, Dursun, & Demircan, 1999), and excessive iron ions in water will pollute the environment. For example, the criterion of iron in drinking water is 0.3 mg/L in China, and excess iron will debase

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the taste of water. On the other hand, excess Fe(III) ions in human blood are toxic to tissues and organs (Burke et al., 2002). Therefore, it is indispensable to remove the excessive Fe(III) ions in water. For this sake, Fe(III) ion was chosen for the evaluation on the adsorption behavior of metal ions onto CMCts gels.

2. Experiment

2.1. Materials

N,O-carboxymethylated chitosan (CMCts) used in this study was obtained from Jinhu Co. Ltd., China, and used as received. The degree of deacetylation (DDA), the degree of substitution (DS) and the weight average molecular weight (M_w) of the CMCts are 90.0%, 1.78 and 5.45×10^4, respectively. Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), sodium chloride, hydrochloric acid and sodium hydroxide used in this experiment were all analytical reagents.

2.2. Preparation of CMCts hydrogels by γ-ray irradiation

CMCts was dissolved in deionized water, and the paste-like homogenous mixtures were obtained after being heated at 60 °C and stirred for about 1 h. Then the mixtures were irradiated at room temperature by ^{60}Co source to form CMCts hydrogels.

2.3. Gel fraction and swelling behavior of crosslinked CMCts hydrogels

The gel content of CMCts hydrogels was determined after removing the soluble part by extraction at 25 °C in deionized water for 4d. The gel fraction (g) equates to the ratio between the weight of the dried gel and the initial weight of CMCts:

$$g(\%) = \frac{G_d}{G_i} \times 100 \tag{1}$$

where G_d is the weight of dry gel after removing sol, and G_i is the initial weight of CMCts.

The hydrogels with certain weight were immersed into deionized water, and then taken out to weigh after a certain time. The swelling degree was calculated according to the following equation:

$$\text{Swelling degree} = \frac{G_t - G_d}{G_d} \tag{2}$$

where G_t is the weight of the hydrogel at time t.

After the equilibrium state of swelling was reached, the equilibrium degree of swelling (EDS) was calculated according to Eq. (2), and here G_t is the weight of the hydrogel in equilibrium state of swelling.

2.4. FTIR analysis

The CMCts gel after removing sol part was analyzed by FTIR. The spectra of the samples were taken in the solid state using potassium bromide pellets with VECTOR22 FTIR spectrometer.

2.5. Adsorption experiments of Fe(III) ions

Stock solution of Fe(III) ions (1000 ppm) was prepared using $FeCl_3 \cdot 6H_2O$. The stock solution was then diluted to make solutions with desired concentrations. Batch adsorption experiments were conducted at room temperature in 250 mL beakers with continuous stirring by a magnetic stirrer. 30–40 mg of the adsorbent (the CMCts gels) was immersed in 200 mL solution. After filtration, the concentrations of Fe(III) ions were analyzed by UV–Vis spectrophotometry at 425 nm wavelength using 5-sulfo salicylic acid as the chromogenic agent.

Effect of pH on Fe(III) ion adsorption was investigated in the pH range of 1.0–6.3 in solution with initial Fe(III) ion concentration of 3.5 ppm. The pH of the initial solution was adjusted using 0.10 mol/L HCl and 0.10 mol/L NaOH. The CMCts gel after removing sol was equilibrated at the certain pH for about 2 h before the addition of Fe(III) ions. Effect of ionic strength (as NaCl) on adsorption of Fe(III) ions was also studied by adding different amount of NaCl to 3.5 ppm Fe(III) ion solution, and the ionic strength (I) was calculated by the concentration of NaCl:

$$I(\text{mol/kg}) \overset{\text{def}}{=} \frac{1}{2} \Sigma m_B z_B^2 \tag{3}$$

where m_B (mol/kg) is the mass molar concentration and z_B is the electrovalence of ion B.

3. Results and discussion

3.1. Radiation-induced synthesis and swelling behavior of CMCts hydrogels

3.1.1. Gel fraction of CMCts hydrogels

γ-ray radiation-induced crosslinking of CMCts was observed at paste-like state with the concentration of CMCts from 12% to 22%. The influence of CMCts concentration and absorbed dose on gel fraction of CMCts hydrogels was shown in Fig. 1. Gel fraction was only about 5% when the concentration of CMCts was 12%, and increased with the increasing of CMCts concentration till about 33% in 20% CMCts aqueous solution. However, when the concentration of CMCts increased to a high value, i.e. 22%, low gel fraction was obtained because CMCts and water could no longer form homogeneous mixture.

In our previous work, radiation-induced change of CMCts in solid state and dilute aqueous solution under the irradiation of ^{60}Co source have been investigated in detail. CMCts primarily undergoes radiation degradation in solid state because of its rigid chains (Huang et al., 2007a). The incorporation of water into CMCts system should be advantageous for the crosslinking of CMCts because the radiolysis of water provides active species to induce more CMCts macroradicals by indirect effect. Moreover, the presence of water enhances the mobility of CMCts molecular chains. Hence, CMCts macroradicals are easier to combine with each other to form the network structures than that in solid state. However, in the dilute CMCts aqueous solutions, the concentration of CMCts macroradicals formed under irradiation is too low to combine with each other (Huang et al., 2007b), so a critical concentration of CMCts is required for their crosslinking reaction. In this study, it

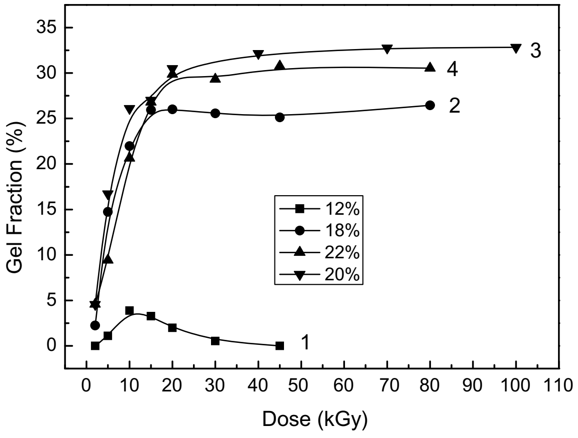

Fig. 1. Gel fractions of CMCts hydrogels synthesized by γ-ray irradiation with different concentrations. 1–12%; 2–18%; 3–20%; 4–22%.

was found that the concentration of 18–20% CMCts is preferable to form CMCts hydrogels.

From Fig. 1 it also can be found that the gel fraction increased quickly with the increase of the dose from 0 to 20 kGy, and then leveled off at high dose. This is because more CMCts macroradicals were formed for crosslinking of CMCts at higher dose. However, for the low concentration solution (12%), chain scission of CMCts occurred obviously when CMCts was irradiated by high dose, causing the decreasing of gel fraction.

3.1.2. Swelling behavior of CMCts hydrogels

The hydrogels synthesized from 18% CMCts solution with 40 kGy irradiation were used for swelling study. The results were shown in Fig. 2. The swelling of CMCts hydrogels was fast in the initial 4 h, and then slowed down gradually. The swelling interval of CMCts hydrogels to equilibrium was about 60 h.

Schott (Schott, 1992) advanced second order kinetics model to describe the swelling process:

$$\frac{dS}{dt} = k_S(S_\infty - S)^2 \tag{4}$$

With initial condition $t = 0$, $S = 0$, it can be used as

$$\frac{t}{S} = A + Bt \tag{5}$$

where k_S is the rate constant of swelling, t is the swelling time, S is the swelling degree, and S_∞ is the theoretically maximum swelling degree. $A = \frac{1}{k_S S_\infty^2} = \frac{1}{(dS/dt)_0}$, which is the reciprocal of initial swelling rate (r_0). B is the reciprocal of S_∞. With the curve of $t/S \sim t$ (inset *a* of Fig. 2, $R^2 = 0.9994$), r_0, S_∞ and k_S were calculated to be 275.7 h^{-1}, 271.7, and 0.00373 h^{-1}, respectively. And the value of S_∞ corresponded well to the result of the experiment, 271.4.

The following equation was usually used to describe the initial part of swelling process ($S/S_\infty \leqslant 60\%$) (Hu & Chou, 1996; Saraydin & Caldiran, 2001):

$$F = \frac{S}{S_\infty} = kt^n \quad \text{or} \quad \ln F = K + n \ln t \tag{6}$$

where k is the swelling coefficient, which is correlative to the network structure of polymer. n is the swelling exponent, from which we can deduce the diffusing behavior of water in the hydrogel. With the curve of $\ln F \sim \ln t$ (inset *b* of Fig. 2, $R^2 = 0.9864$), n was obtained to be 0.49 (<0.5). Therefore, the diffusion behavior of water in CMCts hydrogels could be deduced to be Fickian diffusion. Because of the typical porous structure of CMCts hydrogels, the diffusing rate of water molecules in the CMCts hydrogels is much slower than the relaxation rate of the CMCts chains. Thus the diffusion of water molecules determines the swelling process, and it leads to be Fickian diffusion.

It is well known that pH effect can be observed on the swelling or deswelling of polyelectrolyte gels. In this work, pH-sensitivity of CMCts hydrogels was investigated in a series of solutions with different pH, which were adjusted by 0.1 mol/L HCl and 0.1 mol/L NaOH. The effect of pH on the swelling of CMCts (18%, 40 kGy) hydrogels was shown in Fig. 3. The CMCts hydrogels displayed characteristic pH-sensitivity in swelling behavior, for instance, it deswelled in the pH range $2.0 < pH < 4.0$, and swelled when $pH < 2.0$ or >4.0.

Because the CMCts gels contain both carboxyl and amino groups, it is assumed that the CMCts has an isoelectric point (p_I) like protein molecules. The p_I should be in the pH range of 2.0–4.0, respecting to the content of carboxyl and amino groups in CMCts molecules. In pH 2.0–4.0, most of the ionic groups are absent due to protonation of the carboxyl groups and deprotonation of the amino group, so that CMCts gels thus deswelled in this region.

The ionic strength of swelling surroundings was adjusted by NaCl, and the ionic strength (I) was calculated by Eq. (3) with the concentration of NaCl. The effect of inorganic salt on the swelling of CMCts hydrogels (18%, 40 kGy) was also shown in Fig. 3. Swelling of the CMCts hydrogels showed a typical behavior of polyelectrolyte under different ionic strength that the hydrogels deswelled with the increasing of NaCl concentration especially at the low value ($I < 0.1$ mol/kg). NaCl added into the swelling surrounding would decrease the hydration of CMCts and weaken the osmotic pressure between interior and exterior parts of the hydrogels, which was the main reason of swelling. Hence CMCts hydrogels deswelled.

3.2. FTIR and sol-gel analysis of CMCts gels

Fig. 4 showed the FTIR spectra of uncrosslinked and crosslinked CMCts. In curve a (uncrosslinked CMCts), the strong, broad band at 3440 cm^{-1} ascribed to the ν(O—H) and ν(N—H); the double peaks at 2925 and 2868 cm^{-1} were assigned to the ν_{as}(C—H) and ν_s(C—H); the strong absorption band at about 1602 cm^{-1} corresponded to δ(N—H) of —NH_2 groups and ν(C=O) of —COO^- groups (the little shoulder peak at high wavenumber might be assigned to the carbonyl groups of —CONH—); 1417 cm^{-1} was due to $\delta(CH_2)$ and $\delta(CH_3)$; 1324 cm^{-1} ascribed to ν(C—N) and δ(N—H); 1070 cm^{-1}

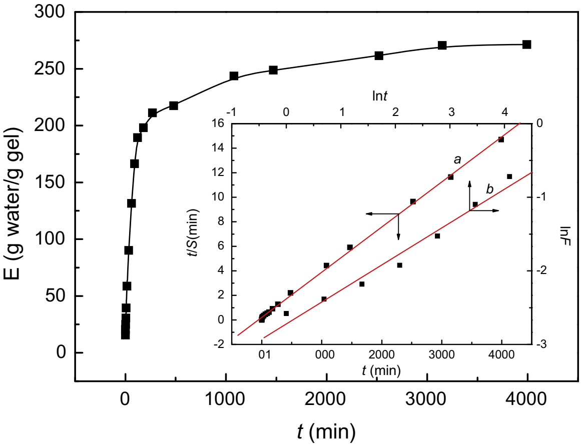

Fig. 2. Swelling kinetics of CMCts hydrogels synthesized by irradiation of 18% CMCts sample at 40 kGy. Inset: the curve of $t/S \sim t$ (*a*), the curve of $\ln F \sim \ln t$ (*b*).

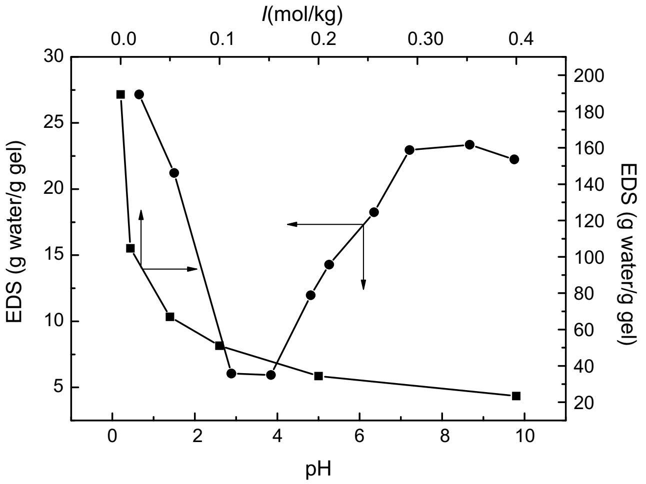

Fig. 3. Effect of pH and ionic strength on the swelling of CMCts hydrogels synthesized by irradiation of 18% CMCts sample at 40 kGy.

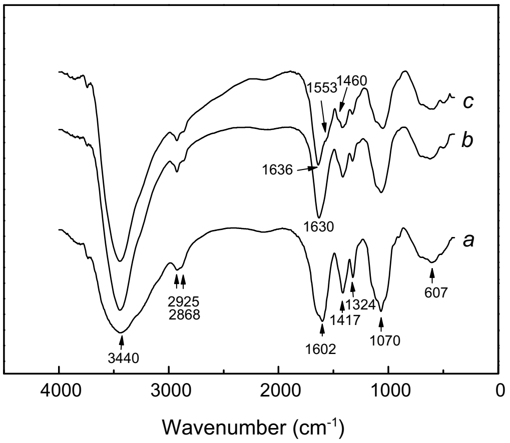

Fig. 4. FTIR spectra of uncrosslinked and crosslinked CMCts. a, uncrosslinked CMCts; b, crosslinked CMCts gel irradiated at 10 kGy; c, crosslinked CMCts gel irradiated at 30 kGy.

was caused by ν(C—O) of C—O—C bonds (Chen & Park, 2003; Dong, Wang, Wu, & Ruan, 2001; Huang et al., 2007b; Sun & Wang, 2006). In the FTIR spectra of crosslinked CMCts (curves *b* and *c*), a change of the band at 1602 cm^{-1} was observed, i.e. the band at 1602 cm^{-1} diminished and the band at high wavenumber appeared (*b*, 1630 cm^{-1}; *c*, 1636 cm^{-1}), which was similar to that of radiation degraded CMCts (Huang et al., 2007b). It revealed that although CMCts were crosslinked after irradiation, radiation degradation also occurred in the process so that new carbonyl groups formed and some $—NH_2$ were scissored out. Meanwhile, the intensity of the band at 1417 cm^{-1} of crosslinked CMCts was diminished comparing with that of uncrosslinked CMCts. It has been reported that the radicals formed in the side chain ($R—O—\dot{C}H—COO^-$) of carboxymethylated cellulose (CMC) took an important role in formation of the CMC gel, which would lead to decrease in intensity of absorption band at 1420 cm^{-1} (Wach, Mitomo, Nagasawa, & Yoshii, 2003). Because the structure of CMCts is similar to that of CMC, the diminishment of 1417 cm^{-1} band in Fig. 4 can be explained as the analogical reason: the $—CH_2—$ groups in the side chain were easy to activate and react with other radicals under irradiation, thus the intensity of absorption band at 1417 cm^{-1} decreased after irradiation. In addition, two new bands at 1553 and 1460 cm^{-1} were observed in the spectra of crosslinked CMCts, which was assigned to δ(N—H) of —NHCO— groups in CMCts molecules.

As mentioned above, the main chemical effects on polymers subjected to ionizing irradiation are crosslinking and chain scission. Both processes occur simultaneously and the yields of crosslinking and scission result in the final effect of irradiation (Chapiro, 1962). p_0/q_0 is the parameter that allows the determination of the final results of irradiation and is equal to half of the scission yield/crosslinking yield ratio [$0.5G(s)/G(x)$], where the *G* value is a measure for the efficiency of the radiochemical process and its absorbed dose dependence. If p_0/q_0 is lower, crosslinking occurs more efficiently. The values of p_0/q_0 ratio and gelation dose D_g, the critical dose for gel formation, of the CMCts hydrogels synthesized in different conditions were calculated by sol-gel analysis according to the Charlesby–Pinner equation (Olejniczak, Rosiak, & Charlesby, 1991):

$$s + \sqrt{s} = \frac{p_0}{q_0} + \frac{1}{q_0 P_n D} \tag{7}$$

where *s* is the sol fraction, p_0 and q_0 are degradation density and crosslinking density respectively (the fractions of degraded and crosslinked main-chain units per unit dose), P_n is the number average of the polymerization degree, and *D* is the absorbed dose. The gelation data were analyzed using a customized computer program (free software **GelSol95** available at http://mitr.p.lodz.pl/biomat/gelsol.html). The calculated results from Fig. 1 were listed in Table 1.

According to the calculated results, it was apparent that the values of p_0/q_0 were all higher than 1. It is revealed that although crosslinked CMCts hydrogels could be prepared by γ-ray radiation method, the rate of radiation degradation of CMCts was faster than that of radiation crosslinking due to the character of CMCts itself, and it corresponded to the results of FTIR. By comparing the p_0/q_0 values of samples 1, 2, 3 and 4, the effect of CMCts concentration was further substantiated that at certain range, higher concentration (18–20%) of homogenous CMCts paste-like solution was favorable to crosslinking. But extremely high concentration of CMCts (22%) would counteract crosslinking.

Compared to the work of Yoshii et al. (Zhao et al., 2003), the gelation doses of CMCts in this study were obviously lower, showing that CMCts in our system was easier to crosslink than theirs, though the p_0/q_0 values were lower. It was supposed that there were two aspects of reasons. One was that CMCts in this study had different DDA, DS and M_w with that of Yoshii's, and the structure and molecular weight of CMCts might be have some influence on radiation-induced crosslinking of CMCts. Another attributed to using γ-ray with higher penetrability and lower dose rate in this work. So γ-ray is better than electron beam for the crosslinking of CMCts.

3.3. Adsorption behavior of Fe(III) ions onto CMCts gels

The gels synthesized by γ-induced crosslinking of 20% CMCts sample at 40 kGy owing to their good mechanical properties and swelling behavior were chosen as the adsorbents of Fe(III) ions in the following experiments.

The adsorption kinetic experiment was conducted to determine the optimum condition for the adsorption of Fe(III) ions onto CMCts gels. The results (Fig. 5) showed that the adsorption rate of Fe(III) ions was very fast, and the adsorption amount of Fe(III) ions per unit weight of the gel (*q*) reached the maximum after ca. 20 min. Compared to the results of other metal ion adsorption

Table 1
p_0/q_0 and D_g of CMCts gels calculated according to the Charlesby–Pinner equation

Sample	1	2	3	4
c(CMCts) (%)	12	18	20	22
p_0/q_0	1.92	1.53	1.46	1.47
D_g (kGy)	3.09	2.61	2.59	3.69

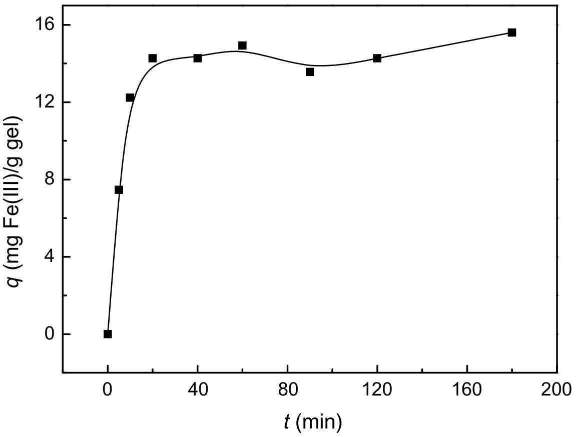

Fig. 5. Adsorption kinetics of Fe(III) ions onto CMCts gels synthesized by irradiation of 20% CMCts sample at 40 kGy.

experiments onto CMCts gels (Wasikiewicz et al., 2005), which cost at least 120 min to reach the maximum adsorption, the CMCts gel was a kind of highly efficient adsorbent for Fe(III) ions due to the high coordination ability of Fe(III) ions with amino, hydroxyl and carboxyl groups of the CMCts molecules. Therefore, in order to achieve the saturated adsorption, 3 h was used as the adsorption time in all following experiments.

A series of adsorption experiments of Fe(III) ions onto CMCts gels were carried out with different pH, ionic strength, concentration of Fe(III) ions, respectively. The effect of pH on the adsorption of Fe(III) ions onto CMCts gels was shown in Fig. 6. Adsorption capacity increased with increasing pH of the solution, and reached the maximum adsorptions at pH 4.7. When pH is less than 2.0, $—NH_2$ groups in CMCts molecules are protonated to form $—NH_3^+$ groups. Thus, the number of free electron pairs on nitrogen atoms of CMCts molecules decreases, reducing the number of coordination sites for Fe(III) ions. In pH 2.0–4.0, CMCts gels deswelled and Fe(III) ions only could be absorbed onto their surface, because most of the ionic groups are absent due to protonation of the $—COO^-$ groups and deprotonation of the $—NH_3^+$ group. So at pH is less than 4.0, the adsorption capacity of Fe(III) ions onto CMCts gels is low. When pH was larger than 4.0, the adsorption capacity of Fe(III) ions onto CMCts gels increases with pH. Moreover, the color of the solution was also changed from colorless to light yellow at pH > 4.0, revealing that $Fe(OH)_3$ micelles charged positive were formed, which could adhere to CMCts gels due to the electrostatic attraction. However, when pH was higher than 7.0, the deposition of $Fe(OH)_3$ inhibited the adsorption distinctly.

Fig. 6 also showed the effect of ionic strength on the adsorption behavior of Fe(III) ions onto CMCts gels. It could be seen that ionic strength affected slightly the adsorption behavior at low NaCl concentration ($I < 0.003$ mol/kg), but when the ionic strength increased, the adsorption capacity decreased obviously. This can be explained from two aspects: (1) although incorporation of NaCl into CMCts gel systems can improve the electrostatic attraction of $—COO^-$ groups in CMCts for the adsorption of metal ions, it also destroys the covalent binding of CMCts and metal ions, which is the main factor of adsorption of metal ions onto CMCts gels (Zhao, Mitomo, Yoshii, & Kume, 2004), thus, the high rate constant of adsorption will decrease; (2) the affinity between NaCl and H_2O enhances with the addition of NaCl, which leads to the decrease of ionic mobility of metal ions (Sun & Wang, 2006). As a result, the addition of NaCl counteracted the adsorption of Fe(III) ions onto CMCts gels.

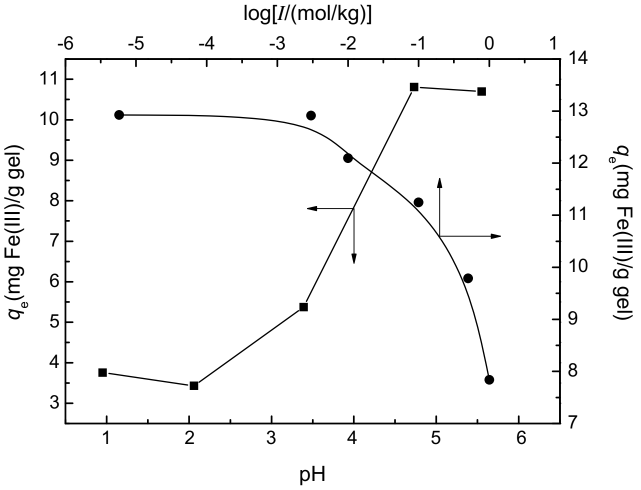

Fig. 6. Effect of pH and ionic strength on the adsorption of Fe(III) ions onto CMCts gels synthesized by irradiation of 20% CMCts sample at 40 kGy.

Fig. 7 showed the experimental equilibrium isotherm of the adsorption of Fe(III) ions onto the CMCts gels. The adsorption capacity increased quickly with the equilibrium concentration of Fe(III) ions at low level, and gradually leveled off when the equilibrium concentration of Fe(III) ions reached ca. 4 ppm. The Langmuir and Freundlich models are often used to describe the isotherms of equilibrium adsorption. The Langmuir equation is valid for homogeneous and monolayer adsorption onto a surface with a finite number of identical sites, and is given by:

$$\frac{C_e}{q_e} = \frac{C_e}{Q} + \frac{1}{Qb} \tag{8}$$

where Q is the maximum adsorption at monolayer (mg/g), C_e is the equilibrium concentration of Fe(III) ions (ppm), q_e is the adsorption amount of Fe(III) ions per unit weight of CMCts gels at equilibrium concentration, and b is the Langmuir constant related to the affinity of binding sites (mL/mg) and is a measure of the energy of adsorption. With the slope and intercept of the linearized plot of C_e/q_e against C_e, Q and b can be calculated.

Freundlich model is an empirical model based on adsorption on a heterogeneous surface. The equation is given by:

$$\log q_e = \log K + \frac{1}{n}\log C_e \tag{9}$$

where K (mg/g) and n, which can be calculated from a linear plot of $\log q_e$ against $\log C_e$, are Freundlich constants indicating adsorption capacity and intensity, respectively.

The linearized forms of the Langmuir and Freundlich isotherms were shown in the inset of Fig. 7. The correlating coefficients (R) calculated by Langmuir and Freundlich equations were 0.9907 and 0.9798, respectively, showing that the adsorption of Fe(III) ions on the CMCts gels correlated better with the Langmuir equation compared with the Freundlich equation under the concentration range studied.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless separation constant factor or equilibrium parameter, R_L, which is used to predict if an adsorption system is "favorable" or "unfavorable". With the Langmuir constant b (660.7 mL/mg), the separation factor R_L can be calculated by:

$$R_L = \frac{1}{1 + bC_0} \tag{10}$$

where C_0 is the initial concentration of Fe(III) ions (ppm). The calculated results revealed that the adsorption of Fe(III) ions on CMCts gels is "favorable" because all R_L values were in the range of $0 < R_L < 1$, and high Fe(III) ion concentration was favorable to the

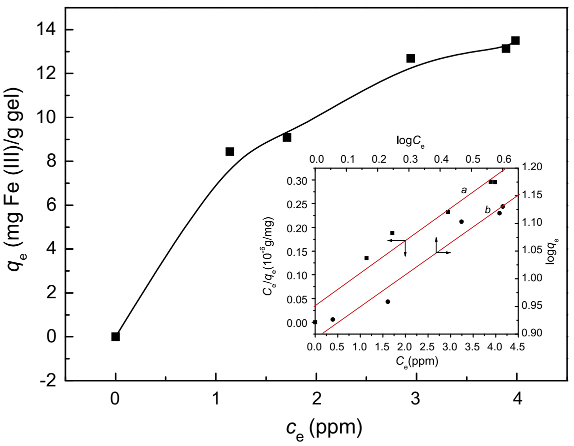

Fig. 7. Adsorption isotherms and linearized forms of the Langmuir and Freundlich isotherms of Fe(III) ion adsorption onto CMCts gels synthesized by irradiation of 20% CMCts sample at 40 kGy. Inset: Langmuir isotherm (a); Freundlich isotherm (b).

adsorption due to the fact that the values of R_L gradually decreased from 0.40 to 0.19 with C_0 increased from 2.28 to 6.36 ppm.

The insoluble porous structures of CMCts gels facilitated the permeating of metal ions. The process of ion adsorption onto the porous adsorbents may involve three steps (Peniche-Covas, Alvarez, & Arguelles-Monal, 1992): (a) diffusion of the ions to the external surface of the adsorbent; (b) diffusion of the ions into the pores of the adsorbent; (c) adsorption of the ions on the internal surface of the adsorbent. In these three steps of adsorption process, the first step may be affected by metal ion concentration, so high Fe(III) ion concentration is favorable to the adsorption, which is proved by R_L values. And the last step is relatively a rapid process.

There has been little study concerning the adsorption mechanism about the Fe(III) ion adsorption onto CMCts gels. Consulting the researches on the Fe(III) ion adsorption onto other adsorbents (Burke et al., 2002) and chelation between amino acid and transition metals (Nyberg & Cefola, 1965), we suppose the adsorption mechanism as follows.

It is assumed that the metal ion is bound by the amino groups, carboxyl groups and hydroxyl groups. Some researches disclosed that the adsorption of Fe(III) ions onto chitosan increased with the amount and degree of deacetylation (DDA) (Burke et al., 2002), which revealed that nitrogen atoms of amino groups had higher coordinating ability than oxygen atoms of carbonyl groups . Considering that five- or six-membered rings is stable, Fe(III) ions are very possible to bind 2-amino groups and 3-hydroxyl groups to form five-membered chelate rings like the adsorption of metal ions on δ-hydroxylysine (Nyberg & Cefola, 1965), which might be the main force of Fe(III) ion adsorption onto CMCts gels. On the other hand, since the steric hindrance, carboxyl groups can only bind to Fe(III) ions solely, which might be the subsidiary forces of the adsorption.

The maximum adsorption capacity (Q) was 18.5 mg/g gel calculated by the Langmuir equation. Compared to the results of chitosan as the adsorbents, although the adsorption capacity of CMCts gels is higher than the results of A. Burke (Burke et al., 2002), it is less than the results of W.S. Wan Ngah (Ngah, Ab Ghani, & Kamari, 2005). Besides the reasons of material characteristics and operation methods, this can be explained by two reasons: (1) adsorption ability is affected obviously by the particle size (Burke, Yilmaz, Hasirci, & Yilmaz, 2002), and small particles possess high adsorption ability due to their large specific surface areas. (2) As mentioned above, amino groups have higher coordinating ability than carbonyl groups. After carboxymethylation, part of amino groups of chitosan is replaced, which leads to low adsorption capacity of Fe(III) ions, but forming carboxyl groups also can enhance its adsorption ability to Fe(III) ions. Therefore, CMCts gels can be used as potential removing materials of Fe(III) ions from aqueous environments.

4. Conclusion

CMCts hydrogels were synthesized successfully by γ-ray irradiation at paste-like conditions. The diffusion behavior of water in the CMCts hydrogel was proved to be Fickian diffusion. Study on Fe(III) ion adsorption onto CMCts gels displayed that adsorption behavior was favorable due to the existence of coordination groups, such as amino, hydroxyl and carboxyl groups, in CMCts structures. The adsorption process was very fast, corresponded well to Langmuir isotherm, and the maximum uptake of Fe(III) ion was determined to be 18.5 mg/g gel.

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