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Removal of Congo red from aqueous solution using *Moringa oleifera* seed cake as natural coagulant

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ABSTRACT

This study investigated the feasibility of *Moringa oleifera* seed cake powder (MOSCP), a natural product after oil extraction, for Congo red (CR) removal from aqueous solution. Coagulation experiments indicated that CR was efficiently removed by MOSCP in short time. Fourier Transform Infrared Spectroscopy spectra showed that large amount of proteins was contained in MOSCP. The removal of CR was contributed to both the adsorption and charge neutralization of proteins on the surface of MOSCP particles, and nucleation of these particles. No significant impact of solution pH was observed on CR removal under acid and neutral conditions, but the CR removal decreased remarkably with increasing pH under basic condition. An optimal MOSCP dosage was found that was linearly proportional to CR initial concentration.

Keywords: *Moringa oleifera* seed cake powder; Congo red; Coagulation; Adsorption; Charge neutralization

1. Introduction

Textile dyes and other industrial dyestuffs are one of the largest groups of organic pollutants that represent increasing attentions. It was estimated by World Bank that 17–20% of industrial water pollution is attributed to textile dyeing and treatments [1]. These dye pollutants are not only a major source of non-aesthetic pollution and eutrophication but also considered to be carcinogenic, mutagenic, and toxic even at low concentrations [2]. Due to the presence of large degree of aromatics in dye molecules and the stability of modern dyes, conventional biological wastewater treatment methods are generally ineffective for their discoloration and degradation. Therefore, a number of physical or chemical methods have been investigated in recent years for dye pollutant removal, such as adsorption [3–12], coagulation–flocculation [13], electrochemical oxidation [14], photocatalytic oxidation [15–17], etc. Among them, coagulation–flocculation is one of most attractive technologies because of its versatility, easy operation, low cost, and less energy consumption [18–20]. Presently, most of commercial coagulants are synthetic, and some of them have negative impact to human health. For example, aluminum chloride or aluminum sulfate may cause Alzheimer's disease [13]. Hence, there is an increasing demand for safe and eco-friendly natural coagulants.

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Moringa oleifera is a tropical plant belonging to the family of Moringaceae, and it has been massively planted in South China such as Yunnan and Sichuan provinces. Recently, it has been reported that *M. oleifera* seed (MOS) is a highly efficient natural product for water treatment to remove turbidity [21], heavy metals [22–24], *Escherichia coli* [25], algae [26,27], and surfactants [28]. As MOS is a good source of edible oil due to its high oil content, it is not appropriate from an economic point of view to use it for wastewater treatment. Most recently, it was reported that *M. oleifera* seed cake (MOSC) that is the residual solids of *M. oleifera* seed after oil is extracted, has similar performance in turbidity removal as MOS [29]. The reason could be that large amount of water soluble proteins is still present in MOSC after oil extraction and the proteins have been proved to be good coagulant for turbidity removal [30]. However, it is still unknown if the MOSC can be applied for dye removal from water.

Congo red (CR) is a benzidine-based dye (1-naphthalenesulfonic acid, 3,3´-(4,4´-biphenylenebis (azo)) bis(4-amino-) disodium salt) prepared by coupling tetrazotised benzidine with two molecules of napthionic acid [31]. It is widely used in textile, paper, printing and dyeing, rubber, plastics and leather industries, etc [32,33]. Once CR containing wastewater is discharged into environment, it can be metabolized to benzidine which is a well-known human carcinogen [34–38]. Moreover, exposure to CR can cause some allergic responses [39]. Due to its popularity, toxic potential, high solubility [32,40,41], it was selected as the model pollutant in the study.

The present study aimed to investigate the feasibility of using MOSC to remove CR from synthetic wastewater. To understand the mechanism of CR removal by MOSC, particularly the role of the water soluble proteins in MOSC, control experiment was also conducted using the MOSC after extracting proteins by $(NH_4)_2SO_4$ and the extracted proteins, respectively. The effects of key operation parameters on CR removal, such as, pH, dosage, temperature, and reaction time, have been systematically studied. The results may be helpful for both CR containing wastewater treatment and application of MOSC in wastewater treatment.

2. Methods

2.1 Preparation of coagulants

The MOSC used in this study was supplied by Yunnan *M. oleifera* Bio-Technique Co. Ltd. In order to investigate the coagulation mechanism, three different coagulants were prepared as follows, respectively: (1) The MOSC was crushed and sieved through 0.45 mm screen. The product was named *M. oleifera* seed cake powder (MOSCP); (2) 1 g of MOSCP was mixed with 100 ml of 1 M $(NH_4)_2SO_4$ solution on a magnetic stirrer at 2,000 rpm for 10 min to extract proteins from MOSCP. Subsequently, the mixture was filtered separated with a 0.45 μm membrane and the solid were washed with distilled water for several times, followed by drying in an oven for 48 h at 40℃. The MOSCP after extracting protein was named as MOSCP-AEP; and (3) In order to reclaim the proteins, fine $(NH_4)_2SO_4$ powder was then added slowly into the filtrate obtained in step (2) on a magnetic stirrer at 2,000 rpm until the saturation of $(NH_4)_2SO_4$ reached 30%. The precipitate was separated by centrifuge at 4,000 rpm for 10 min and then re-dispersed into 10 ml distilled water. The suspension was then put into a dialysis tube with a molecular weight cutoff of 2,000 Da, which was put into 1 L distilled water for dialysis until no white precipitate was observed in the water when adding 1 M $BaCl_2$. The MOSCP extract obtained in the dialysis tube was diluted with distilled water to 100 mL and was denoted as MOSCP-E. The three products were all used as coagulant for CR removal to understand the role of proteins.

2.2 Preparation of artificial wastewater

The CR solution was prepared by adding a certain amount of CR (produced by Ruijinte chemical company, Tianjin, China) into distilled water. The pH of the CR solution was adjusted by 0.1 M KOH and 0.1 M HCl solutions. The pH was measured by a pH meter (pHS-3C, Leici Ltd., China). The solution temperature was determined by a mercury thermometer. All other reagents used in the study were of analytical grade.

2.3 Coagulation experiments

Coagulation experiments were carried out on a Jar-Test apparatus. After the prepared coagulants were added into 500 ml of CR solution, the solution was rapidly mixed (200 rpm) for three minutes and followed by slow mixing (40 rpm) for 15 min [13]. The mixture was then allowed to settle for a predetermined time (15–90 min). Samples about 10 ml were collected periodically from 2 cm below the water surface using a syringe. The samples were then rapidly centrifuged at 4,000 rpm for 5 min. CR concentration in the supernatant was determined by a spectrophotometer (UVmini-1240, Shimadu, Japan) at the wavelength of 500 nm [34,42].

2.4 Infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) was employed to characterize MOSCP, MOSCP-AEP, and MOSCP-E. Potassium bromide pellets were prepared by mixing 1 mg of dried MOSCP or MOSCP-AEP with 200 mg of KBr (spectrometry grade) and then pressing at 10,000 kg/cm for 30 min under vacuum. For the preparation of MOSCP-E sample, a drop of its solution was deposited on a KBr tablet and then the water on the tablet was evaporated at 40℃. The FTIR spectra were recorded on a Nicolet 5,700 FTIR from 4,000 to 400 cm^{-1} and then were analyzed in the amide I–IV spectral regions.

2.5 Image capture

An optical microscope (Nikon Eclipse E200, Japan) equipped with a video camera (Pixelink, PL-A662, Canada) was used to observe the morphology of flocs. After the coagulation experiment was stopped and settled for 30 min, a drop of solution was carefully deposited on a glass slide and covered with a cover slip. The slide was observed immediately and images were taken at a magnification of 100×.

3. Results and discussion

3.1. Infrared spectroscopy

As proteins in MOSCP play important role in water purification, FTIR technique was employed to identify the proteins in the prepared MOSCP, MOSCP-AEP, and MOSCP-E coagulant. Fig. 1(a)–(c) show the FTIR spectra of MOSCP, MOSCP-AEP, and MOSCP-E, respectively. It can be seen that proteins exist in MOSCP as shown in Fig. 1(a). The band at 1,668 cm^{-1} is attributed to the C=O stretching (amide I) [43]. The band at 1,545 cm^{-1} is related with CN stretching and NH bending (amide II) [43]. The bands at 1,272 and 1,237 cm^{-1} are corresponded to the CN stretching (amide III), and the band at 646 cm^{-1} is attributed to OCN bending (amide IV) [43]. The bands at 594 cm^{-1} is related to C=O out-of-plane bending (amide VI) [43]. For the FTIR spectrum of MOSCP-AEP (Fig. 1(b)), the bands at 1,668 and 1,544 cm^{-1} have decreased intensity, the bands at 1,272, 646, and 594 cm^{-1} disappeared, and the band at 1,237 cm^{-1} for MOSCP shifted to 1,241 cm^{-1}. These indicate that proteins have been extracted by $(NH_4)_2SO_4$ solution from MOSCP. For the FTIR spectrum of MOSCP-E, the bands related to proteins are observed as shown in Fig. 1(c). For example, the band at 1,654 cm^{-1} is corresponded to the C=O stretching (amide I). The band at 1,545 cm^{-1} is related with CN stretching and NH bending (amide II). The band at 1,237 cm^{-1} is contributed to the CN stretching (amide III) [43]. These data indicate that the MOSCP-E contained various proteins. Hence, MOSCP-AEP has lower proteins contents than MOSCP and water-soluble protein is the main component of MOSCP-E.

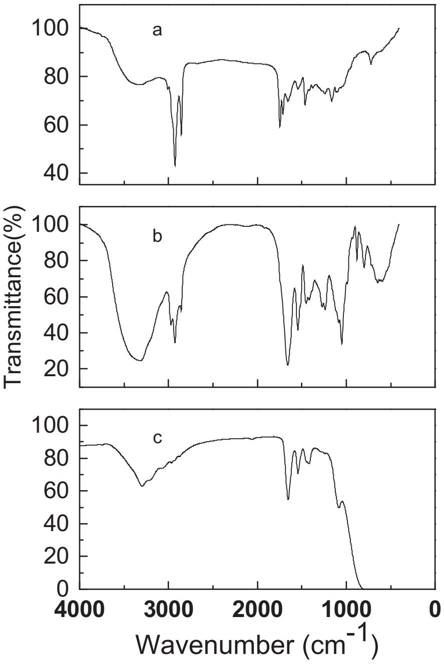

Fig. 1. FTIR spectrum of MOSCP (a), MOSCP-AEP (b), and MOSCP-E (c).

3.2 Effect of different coagulants

The individual performance of MOSCP, MOSCP-AEP, and MOSCP-E used as coagulants in CR removal is shown in Fig. 2(A). It can be seen that 95.8% of CR removal is achieved by MOSCP, which indicates the MOSCP is an excellent coagulant for CR removal. However, MOSCP-AEP and MOSCP-E are less efficient and their CR removals are of only 33.3 and 22.4%, respectively. It is not surprising that MOSCP-AEP has a low performance in CR removal as most proteins have been extracted by $(NH_4)_2SO_4$ solution. However, the low CR removal efficiency of MOSCP-E conflicts with literature. Previous study reported that the water-soluble proteins are excellent coagulants for turbidity removal [30]. The reason why the proteins have different performance in the two studies might be that different pollutants were used. In the present study, the pollutant is CR which is high soluble in water, but suspended solid was the target pollutant in the previous study. The results indicate that proteins

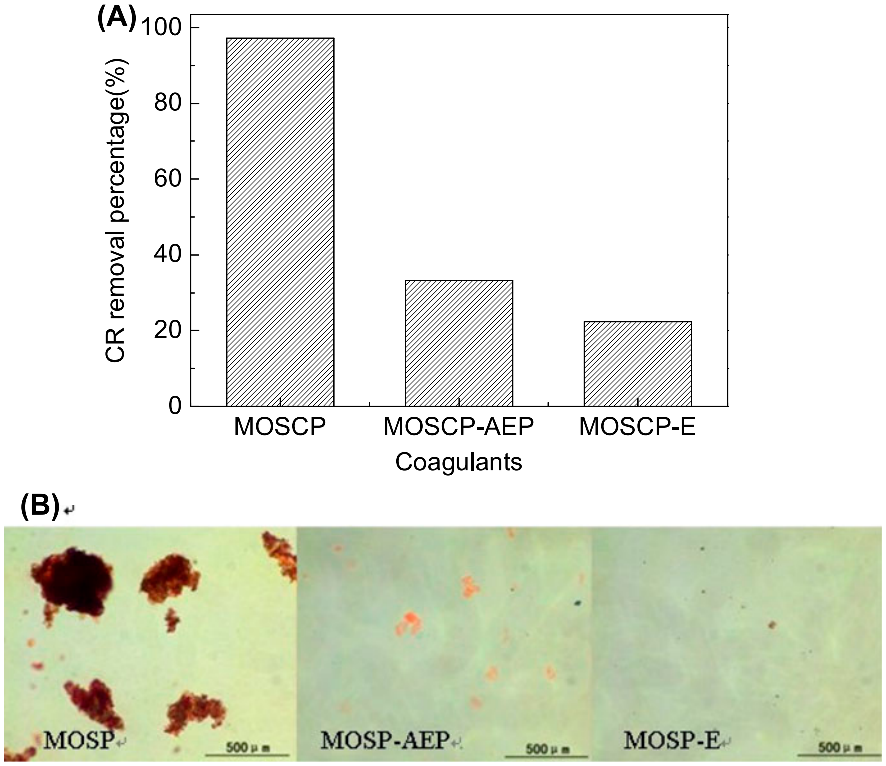

Fig. 2. Effect of three coagulants on CR removal (A) and the microscope photographs of flocs formed by the coagulants (B) (coagulant dosage: MOSCP: 0.16 g/L, MOSCP-AEP: 0.16 g/L, MOSCPE: 8 ml (equals to 0.16 g/L MOSCP), $T = 30 \pm 2$°C, settling time = 0.5 h, $C_0 = 24$ mg/L).

themselves are ineffective for the removal of soluble pollutants.

The microscope photographs of the flocs formed during coagulation–flocculation of CR solution with MOSCP, MOSCP-AEP, and MOSCP-E are shown in Fig. 2(B). It can be seen that the floc size formed by MOSCP is larger than that formed by MOSCP-AEP and the floc formed by MOSCP-E has the smallest size and lowest density. This indicates that larger floc resulted in higher CR removal. The excellent higher CR removal by MOSCP is clearly attributed to both MOSCP particle and protein. At the pH 7.8, set for the experiment, the amino group of proteins on the surface of MOSCP is positively charged [30] while the SO_3^{2-} groups of CR is negatively charged [36,44]. Therefore, CR molecules are electrostatically adsorbed onto the surface of MOSCP forming large flocs. During the process, the MOSCP particles serve as the nuclei for the formation of the flocs. For MOSCP-AEP, fewer CR molecules are adsorbed as it contains less protein, which in turn results in a poor CR removal. By contrast, although the MOSCP-E contains high content of water-soluble proteins, it is difficult to form large flocs due to lack of nuclei sites. So the CR removal mechanism by MOSCP is a combination of adsorption and charge neutralization of the proteins on MOSCP surface and nucleation of the MOSCP particles. Fig. 3 shows the schematic of the removal mechanism. MOSCP was used in the following experiments due to its better performance than MOSCP-AEP and MOSCP-E.

3.3 Effect of settling time, pH, and temperature

The removal efficiency of CR as function of settling time is shown in Fig. 4(A). It can be seen that there is no significant difference in the CR removal efficiency between various settling times from 15 to 90 min for four MOSCP dosages. This indicates that the reaction between the MOSCP and CR has completed during the mixing period and no further reaction occurs between either the MOSCP and CR or the flocs formed and CR during the settling period.

Fig. 4(B) shows the effect of initial pH of the CR solution on its removal. It can be seen that the CR removal retains constant around 97.0% when the pH increases from 4.0 to 9.0, but it dramatically drops to 17.3% as the pH further increases to 11.0. This indicates that the pH of the CR solution plays a very important role in its coagulation process [45]. The rea-

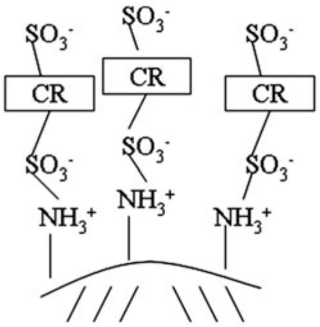

Fig. 3. Schematic illustration of the coagulation mechanism of CR dye with MOSCP.

son might be that pH affects both the degree of ionization and speciation of the CR dye and the surface charge of the MOSCP. It was reported that the isoelectric point of the CR is around 3 [36,44]. Hence, the CR exists mainly in its dissociated form and is negatively charged in the pH range of 3.0–11.0. By contrast, the water-soluble cationic proteins in the MOSCP have isoelectric points between pH value of 10 and 11 [30]. Hence, the MOSCP surface is positively charged at pH values from 3.0 to 9.0. The positively charged MOSCP surface is favorable for the adsorption of the negatively charged CR by electrostatic attraction, resulting in a high CR removal. At pH value of between 10 and 11, the MOSCP surface turns to negatively charged which weakens its electrostatic adsorption of CR, hence leading to a poor CR removal.

The effect of the temperature of the solution on CR removal is shown in Fig. 4(C). CR removal increases from 36.7 to 97.2% as the temperature increases from 12 to 32℃, indicating that low temperature is unfavorable for CR removal. It can be explained from the following aspects: (1) The viscosity of the solution increases with a decline of temperature. The high viscosity of the solution at low temperature can negatively influence the settlement of the flocs [46], leading to a poor CR removal; (2) The aggregation rate of the particles in solution is weakened by low temperature, resulting in a poor CR removal [47]; (3) Additionally, some particles of MOSCP cohered together to form pastes at low temperature. The pastes decrease the total surface areas for the electrostatic adsorption of CR, which in turn leads to the poor performance of MOSCP.

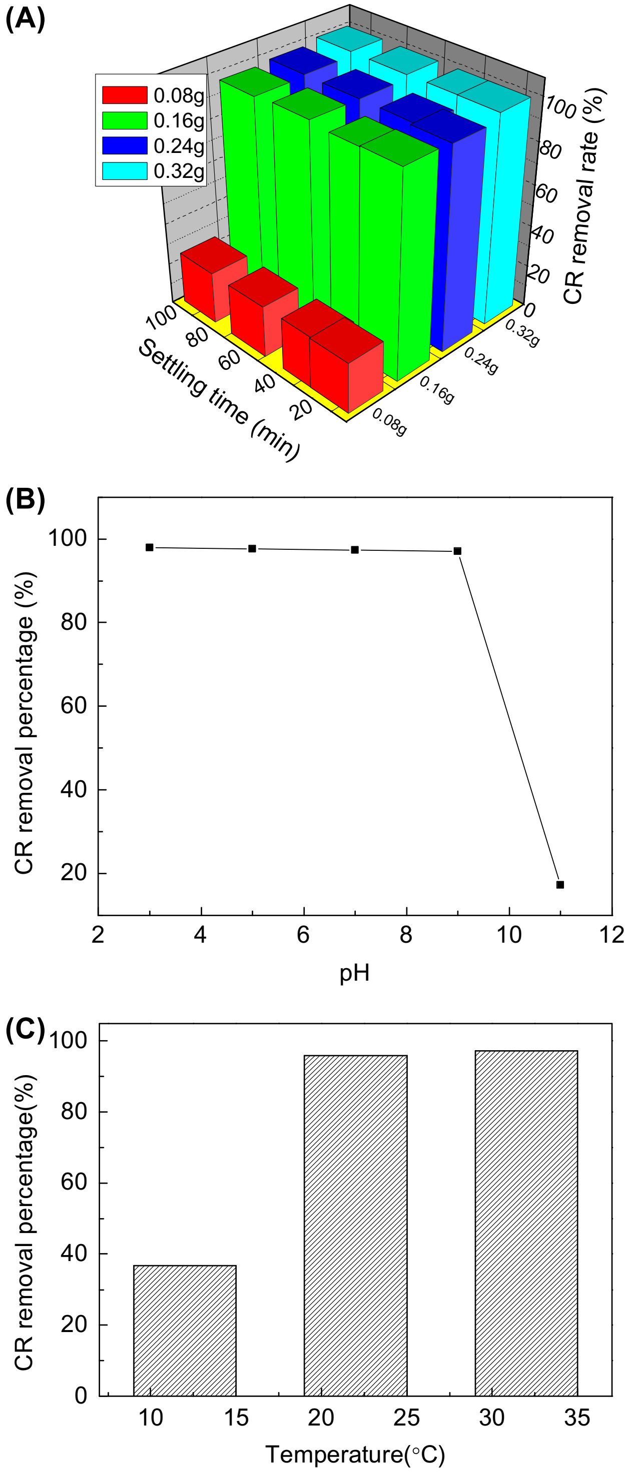

Fig. 4. Effect of settling time (A), pH (B), and temperature (C) on CR removal (A: $C_0 = 13.7$ mg/L, $T = 21 \pm 2$℃; B: $T = 21 \pm 2$℃, $C_0 = 24$ mg/L, MOSCP: 0.16 g/L, settling time = 0.5 h; C: $C_0 = 24$ mg/L, MOSCP: 0.16 g/L, settling time = 0.5 h).

3.4 Effect of MOSCP dosage and CR concentration

In order to investigate the effects of MOSCP dosage and CR concentration on CR removal, the CR removal efficiency was measured varying MOSCP dosage from

0 to 0.52 g/L and CR concentration from 6.6 to 48.0 mg/L, respectively. As shown in Fig. 5(A)–(E), the residual concentration of CR decreases with the increase of MOSCP dosages regardless of CR concentration. It indicates that higher MOSCP dosage results in better CR removal efficiency because higher MOSCP dosage offers more active sites. Interestingly, there exists a saturated MOSCP dosage for each CR initial concentration. After the MOSCP dosage reaches the saturated dosage, further increasing MOSCP can only lead to a very tiny increase in CR removal. In addition, a linear relationship between the CR concentration and the saturated MOSCP dosage was observed as shown in Fig. 5(F), which can be described by the equation

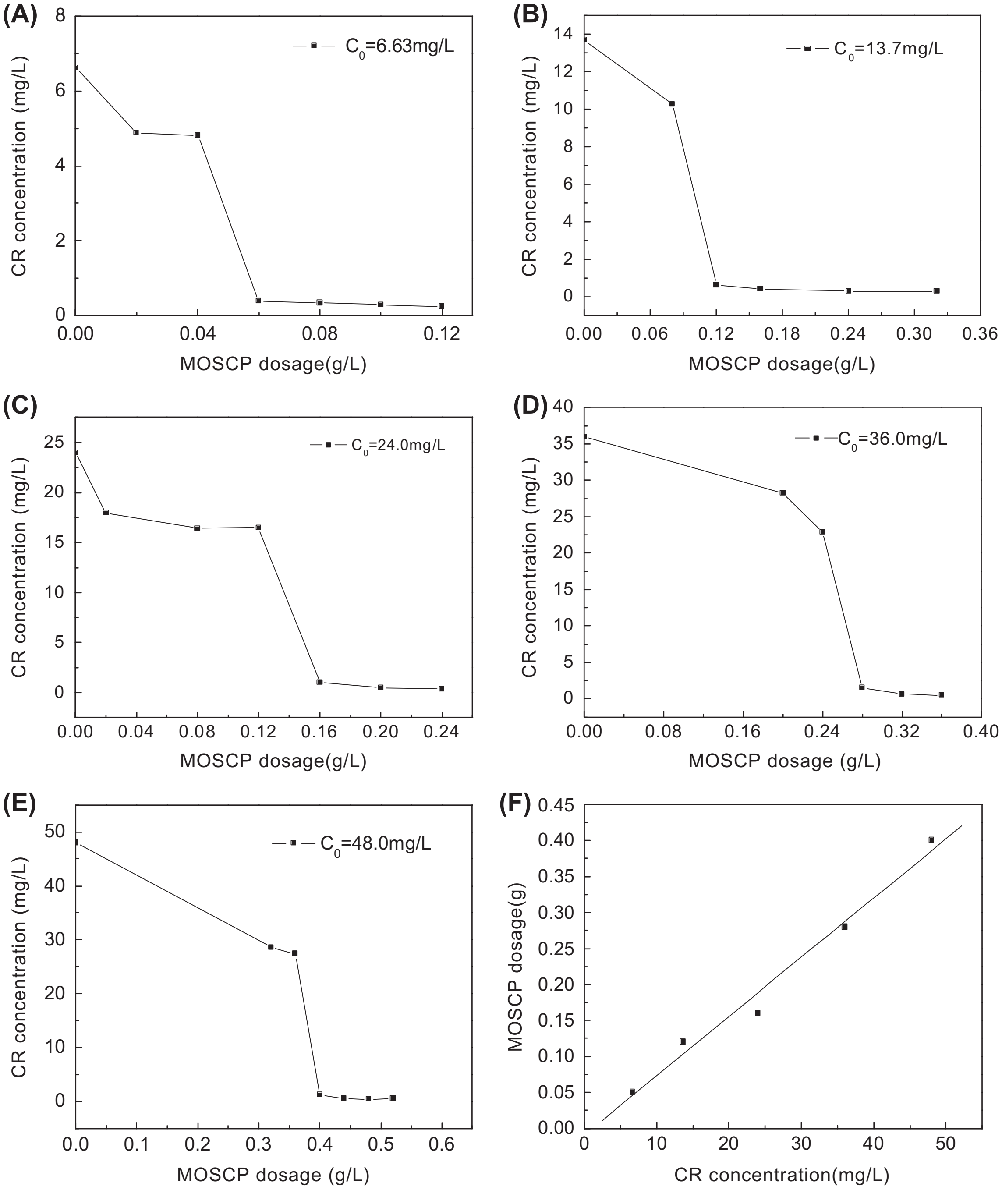

Fig. 5. Effect of MOSCP dosage and CR concentration on CR removal (A–E) and the relationship between CR concentration and saturated MOSCP dosage (F) ($T = 21 \pm 2$°C, settling time = 0.5 h).

$Y = 0.0041x - 0.0046$ ($R^2 = 0.982$, x the CR concentration, Y the MOSCP dosage). As the CR removal increases slightly after the MOSCP exceeds the saturated dosage, it can be used as the optimal dosage in practical application.

4. Conclusion

This study investigated the performance of MOSCP as natural coagulant for CR removal. The results showed that CR removal mechanism was a combination of adsorption and charge neutralization between proteins on the surface of MOSCP particles and CR molecules and the flocculation by MOSCP particles themselves. Settling time and pH under acid and neutral conditions had no significant impact on CR removal, but the CR removal decreased markedly under basic condition. There also existed a saturated MOSCP dosage for different CR initial concentration and a linear relationship was observed between them. High temperature was favorable for CR removal.

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References

[1] S.H.S. Chan, T. Yeong Wu, J.C. Juan, C.Y. Teh, Recent developments of metal oxide semiconductors as photocatalysts in advanced oxidation processes (AOPs) for treatment of dye waste-water, J. Chem. Technol. Biotechnol. 86 (2011) 1130–1158.

[2] X.W. Zhang, G.T. Li, Y.Z. Wang, J.H. Qu, Microwave electrodeless lamp photolytic degradation of Acid orange 7, J. Photochem. Photobiol., A 184 (2006) 26–33.

[3] A. Mittal, V. Thakur, V. Gajbe, Adsorptive removal of toxic azo dye Amido black 10B by hen feather, Environ. Sci. Pollut. Res. 20 (2013) 260–269.

[4] A. Mittal, V. Thakur, J. Mittal, H. Vardhan, Process development for the removal of hazardous anionic azo dye Congo red from wastewater by using hen feather as potential adsorbent, Desalin. Water Treat. 1–3 (2014) 227–237.

[5] J. Mittal, V. Thakur, A. Mittal, Batch removal of hazardous azo dye Bismark brown R using waste material hen feather, Ecol. Eng. 60 (2013) 249–253.

[6] A. Mittal, D. Jhare, J. Mittal, Adsorption of hazardous dye Eosin yellow from aqueous solution onto waste material de-oiled soya: Isotherm, kinetics and bulk removal, J. Mol. Liq. 179 (2013) 133–140.

[7] V.K. Gupta, A. Mittal, D. Jhare, J. Mittal, Batch and bulk removal of hazardous colouring agent Rose bengal by adsorption techniques using bottom ash as adsorbent, RSC Adv. 2 (2012) 8381–8389.

[8] A. Mittal, R. Jain, J. Mittal, M. Shrivastava, Adsorptive removal of hazardous dye Quinoline yellow from waste water using coconut-husk as potential adsorbent, Fresen. Environ. Bull. 19 (2010) 1–9.

[9] A. Mittal, R. Jain, J. Mittal, S. Varshney, S. Sikarwar, Removal of Yellow ME 7 GL from industrial effluent using electrochemical and adsorption techniques, Int. J. Environ. Pollut. 43 (2010) 308–323.

[10] A. Mittal, Removal of the dye, Amaranth from waste water using hen feathers as potential adsorbent, Electron. J. Environ. Agr. Food Chem. 5 (2006) 1296–1305.

[11] A. Mittal, J. Mittal, L. Kupup, Utilization of hen feathers for the adsorption of Indigo carmine from simulated effluents, J. Environ. Prot. Sci. 1 (2007) 92–100.

[12] J. Mittal, D. Jhare, H. Vardhan, A. Mittal, Removal of the dye, Amaranth from waste water using hen feathers as potential adsorbent, Electron. J. Environ. Agr. Food Chem. 5 (2006) 1296–1305.

[13] A. Szyguła, E. Guibal, M. Palacín, M. Ruiz, A.M. Sastre, Removal of an anionic dye (Acid blue 92) by coagulation–flocculation using chitosan, J. Environ. Manage. 90 (2009) 2979–2986.

[14] G.T. Li, J.H. Qu, X.W. Zhang, J.T. Ge, Electrochemically assisted photocatalytic degradation of Acid orange 7 with β-PbO_2 electrodes modified by TiO_2, Water Res. 40 (2006) 213–220.

[15] X. Zhang, G. Li, Y. Wang, J. Qu, Microwave electrodeless lamp photolytic degradation of Acid orange 7, J. Photochem. Photobiol., A 184 (2006) 26–33.

[16] V.K. Gupta, R. Jain, A. Mittal, T.A. Saleh, A. Nayak, S. Agarwal, S. Sikarwar, Photo-catalytic degradation of toxic dye amaranth on TiO_2/UV in aqueous suspensions, Mater. Sci. Eng., C 32 (2012) 12–17.

[17] S.R. Patil, U.G. Akpan, B.H. Hameed, S.K. Samdarshi, A comparative study of the photocatalytic efficiency of Degussa P25, Qualigens, and Hombikat UV-100 in the degradation kinetic of Congo red dye, Desalin. Water Treat. 46 (2012) 188–195.

[18] A.B. Dos Santos, F.J. Cervantes, J.B. van Lier, Review paper on current technologies for decolourisation of textile wastewaters: Perspectives for anaerobic biotechnology, Bioresour. Technol. 98 (2007) 2369–2385.

[19] J.H. Choi, W.S. Shin, S.H. Lee, D.J. Joo, J.D. Lee, S.J. Choi, L.S. Park, Application of synthetic polyamine flocculants for dye wastewater treatment, Sep. Sci. Technol. 36 (2001) 2945–2958.

[20] W. Chu, Dye removal from textile dye wastewater using recycled alum sludge, Water Res. 35 (2001) 3147–3152.

[21] M.E. Sengupta, B. Keraita, A. Olsen, O.K. Boateng, S.M. Thamsborg, G.R. Pálsdóttir, A. Dalsgaard, Use of *Moringa oleifera* seed extracts to reduce helminth egg numbers and turbidity in irrigation water, Water Res. 46 (2012) 3646–3656.

[22] P. Sharma, P. Kumari, M.M. Srivastava, S. Srivastava, Ternary biosorption studies of Cd(II), Cr(III) and Ni(II) on shelled *Moringa oleifera* seeds, Bioresour. Technol. 98 (2007) 474–477.

[23] V.N. Alves, R. Mosquetta, N.M. Coelho, J.N. Bianchin, K.C. Di Pietro Roux, E. Martendal, E. Carasek, Determination of cadmium in alcohol fuel using *Moringa oleifera* seeds as a biosorbent in an on-line system coupled to FAAS, Talanta 80 (2010) 1133–1138.

[24] V. Obuseng, F. Nareetsile, H.M. Kwaambwa, A study of the removal of heavy metals from aqueous solutions by *Moringa oleifera* seeds and amine-based ligand 1,4-bis[N,N-bis(2-picoyl)amino]butane, Anal. Chim. Acta 730 (2012) 87–92.

[25] M. Pritchard, T. Craven, T. Mkandawire, A.S. Edmondson, J.G. O'Neill, A comparison between *Moringa oleifera* and chemical coagulants in the purification of drinking water—An alternative sustainable solution for developing countries, Phys. Chem. Earth 35 (2010) 798–805.

[26] L. Nishi, A.M. Vieira, M. Vieira, M. Bongiovani, F. Camacho, R. Bergamasco, Hybrid process of coagulation/flocculation with *Moringa oleifera* followed by ultrafiltration to remove Microcystis sp. cells from water supply, Procedia Eng. 42 (2012) 865–872.

[27] C.M. Teixeira, F.V. Kirsten, P.C. Teixeira, Evaluation of *Moringa oleifera* seed flour as a flocculating agent for potential biodiesel producer microalgae, J. Appl. Phycol. 24 (2012) 557–563.

[28] J. Beltrán-Heredia, J. Sánchez-Martín, M. Barrado-Moreno, Long-chain anionic surfactants in aqueous solution. Removal by *Moringa oleifera* coagulant, Chem. Eng. J. 180 (2012) 128–136.

[29] L.Y. Ma, Y.Q. Wang, Z.Q. Zhang, Y.P. Zhang, H. Zheng, J. Gan, Q.F. Duan, Water purification effect of *Moringa oleifera* seeds as natural coagulant, Nat. Prod. Res. Dev. 21 (2009) 483–485, 389 (in Chinese).

[30] A. Ndabigengesere, K.S. Narasiah, B.G. Talbot, Active agents and mechanism of coagulation of turbid waters using *Moringa oleifera*, Water Res. 29 (1995) 703–710.

[31] M.K. Purkait, A. Maiti, S. DasGupta, S. De, Removal of Congo red using activated carbon and its regeneration, J. Hazard. Mater. 145 (2007) 287–295.

[32] R.P. Han, D.D. Ding, Y.F. Xu, W.H. Zou, Y.F. Wang, Y.F. Li, L.N. Zou, Use of rice husk for the adsorption of Congo red from aqueous solution in column mode, Bioresour. Technol. 99 (2008) 2938–2946.

[33] B. Cheng, Y. Le, W. Cai, J. Yu, Synthesis of hierarchical $Ni(OH)_2$ and NiO nanosheets and their adsorption kinetics and isotherms to Congo red in water, J. Hazard. Mater. 185 (2011) 889–897.

[34] L. Wang, A.Q. Wang, Adsorption properties of Congo red from aqueous solution onto N,O-carboxymethyl-chitosan, Bioresour. Technol. 99 (2008) 1403–1408.

[35] I.D. Mall, V.C. Srivastava, N.R. Agarwal, I.M. Mishra, Removal of Congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses, Chemosphere 61 (2005) 492–501.

[36] R. Ahmad, R. Kumar, Adsorptive removal of Congo red dye from aqueous solution using bael shell carbon, Appl. Surf. Sci. 257 (2010) 1628–1633.

[37] A. Afkhami, R. Moosavi, Adsorptive removal of Congo red, a carcinogenic textile dye, from aqueous solutions by maghemite nanoparticles, J. Hazard. Mater. 174 (2010) 398–403.

[38] A. Mahapatra, B.G. Mishra, G. Hota, Adsorptive removal of Congo red dye from wastewater by mixed iron oxide–alumina nanocomposites, Ceram. Int. 39 (2013) 5443–5451.

[39] S. Chatterjee, M.W. Lee, S.H. Woo, Adsorption of Congo red by chitosan hydrogel beads impregnated with carbon nanotubes, Bioresour. Technol. 101 (2010) 1800–1806.

[40] V. Vimonses, S.M. Lei, B. Jin, C.W.K. Chow, C. Saint, Adsorption of Congo red by three Australian kaolins, Appl. Clay Sci. 43 (2009) 465–472.

[41] V.S. Mane, P.V. Vijay Babu, Kinetic and equilibrium studies on the removal of Congo red from aqueous solution using Eucalyptus wood (*Eucalyptus globulus*) saw dust, J. Taiwan Inst. Chem. Eng. 44 (2013) 81–88.

[42] L. Wang, A.Q. Wang, Adsorption properties of Congo red from aqueous solution onto surfactant-modified montmorillonite, J. Hazard. Mater. 160 (2008) 173–180.

[43] J. Kong, S.N. Yu, Fourier transform infrared spectroscopic analysis of protein secondary structures, Acta Biochim. Biophys. Sin. 39 (2007) 549–559.

[44] Z.Y. Zhang, Congo red adsorption by ball-milled sugarcane bagasse, Chem. Eng. J. 178 (2011) 122–128.

[45] B. Shi, G. Li, D. Wang, C. Feng, H. Tang, Removal of direct dyes by coagulation: The performance of preformed polymeric aluminum species, J. Hazard. Mater. 143 (2007) 567–574.

[46] T.R. Camp, D.A. Root, B.V. Bhoota, Effects of temperature on rate of floc formation, J. Am. Water Works Assoc. 11 (1940) 1913–1927.

[47] F. Xiao, J.-C.H. Huang, B.J. Zhang, C.W. Cui, Effects of low temperature on coagulation kinetics and floc surface morphology using alum, Desalination 237 (2009) 201–213.