Removal of an anionic azo dye direct black 19 from water using white mustard seed (*Semen sinapis*) protein as a natural coagulant

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ABSTRACT

In this study, standard jar tests were conducted using white mustard seed protein (WMSP) as a natural coagulant to remove direct black 19 (DB-19) from its aqueous solution. Comparative coagulation tests were performed using commercial polyaluminum (PAC) chloride (PAC). The results showed that DB-19 removal by WMSP increased with increasing settling time and reached the maximum removal at 180 min. The DB-19 removal descended from 98.4 to 46.2% as pH increased from 4 to 10. The most effective temperature for DB-19 removal was 25 °C. The removal of DB-19 was weakened by the presence of $Na_2S_2O_4$. Overall, WMSP was more efficient than PAC for DB-19 removal in all experiments except at pH 4 and 5. The mechanism of the removal of DB-19 by WMSP could be attributed to adsorption and charge neutralization processes.

Key words | coagulation, direct black 19, polyaluminum chloride, white mustard seed protein

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INTRODUCTION

Globally, the textile industry is one of the largest fresh water consumers which consequently generates large amounts of wastewater. According to the data of the China statistical yearbook on the environment, the textile industry discharged 1.84×10^9 tons of wastewater in 2015, ranking as the third largest pollutant source among the 41 types of industries under investigation. The dyeing wastewater contains a large variety of contaminants including salts, dyes, heavy metals, surfactants, soaps, enzymes, oxidizing, reducing agents, and so on (Verma *et al.* 2012b; Bilińska *et al.* 2017; Costa *et al.* 2018). Among the pollutants, the residual dyes are the most peremptory sources of contamination

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since they are aesthetically undesirable, and can damage the aquatic ecosystem significantly by blocking light penetration and preventing oxygen transfer (Shi *et al.* 2007; Verma *et al.* 2012b; Lafi *et al.* 2018). Furthermore, most of the dyes used in the textile industry are synthetic and belong to azo derivatives, which make them and their metabolite products mutagenic and carcinogenic (Weisburger 2002; Bashiri *et al.* 2018). As a result, it is of great importance to remove the dyes from wastewater.

So far, many techniques have been developed to treat dyeing wastewater. For example, biological processes, coagulation/flocculation, adsorption and advanced oxidation processes including ozonation and photocatalytic reaction, etc. (Tie *et al.* 2016; Bilińska *et al.* 2017; Wang *et al.* 2017, 2018; Mahmoodi *et al.* 2018; Yan *et al.* 2018). Among the techniques, coagulation/flocculation has many advantages such as cost effectiveness, convenience in operation, low energy consumption, and no generation of harmful and toxic intermediates (Shi *et al.* 2007; Verma *et al.* 2012a).

Currently, the commercial coagulants used for water treatment consist of two major groups, namely, inorganic coagulants and organic polymers. Though both of them are playing a very important role in water treatment, many drawbacks arise in water treatment, such as inefficiency at low temperature, changes of pH, corrosion of instruments, and generation of a huge amount of non-biodegradable sludge and so on. Furthermore, their residuals in water can cause adverse impacts on living beings. For example, studies revealed that aluminum is neurotoxic and can cause pathogenesis of Alzheimer's disease (Flaten 2001; Polizzi *et al.* 2002). Also, the residual monomers of polyacrylamide (PAM) present in treated water have been proven to be neurotoxic and carcinogenic (Šciban *et al.* 2009). Hence, the development of eco-friendly coagulant has been a major topic of research in water treatment.

Plant-based coagulants, including mustard seed, *Jatropha curcas* seed, guar gum, copra, *Cactus latifaria*, *Prosopis juliflora* seed, common bean, chitosan, orange waste and so on, have been used to remove a large variety of pollutants including turbidity, algae, dyes, humic acid, bacteria and metals etc. from water due to their advantages such as abundant source, high efficiency, low sludge production, biodegradability, and nontoxicity (Pritcharda *et al.* 2010; Antov *et al.* 2012; Abidin *et al.* 2013; Banerjee *et al.* 2013; Fatombi *et al.* 2013; Bodlund *et al.* 2014; Tie *et al.* 2015; Chethana *et al.* 2016; Ferhat *et al.* 2016; Tie *et al.* 2017; Kebaili *et al.* 2018).

For instance, Ndabigengesere *et al.* (1995) reported that the active agents in aqueous *Moringa* extracts were cationic proteins with a molecular weight of 13 kDa and an isoelectric point between 10 and 11. The optimal dosage of shelled *Moringa oleifera* seed was almost the same as alum, whereas purified proteins were more effective than alum for turbid water treatment. Furthermore, the innocuous coagulant did not affect the pH and conductivity of treated water with four or five times less volume of chemical sludge created compared to alum.

Recently, Boulaadjoul *et al.* (2018) reported that *Moringa oleifera* seed powder was used to enhance the primary treatment of paper mill effluent. The results indicated that the turbidity and COD abatements were 96.02 and 97.28% using *Moringa oleifera* seed powder as coagulant, whereas the respective removals of turbidity and COD by alum were 97.1 and 92.67%, indicating that *Moringa oleifera* is a very efficient natural coagulant for the treatment of paper mill effluent.

Betatache *et al.* (2014) reported that the optimum dosage of prickly pear cactus was 0.4 g/kg for sewage sludge conditioning, which was much more efficient than three polyelectrolytes, namely, 0.8 g/kg for Chimfloc C4346, 80 g/kg for $FeCl_3$ and 60 g/kg for $Al_2(SO_4)_3$.

In recent research, mustard seed proteins with the molecular weight of approximately 6.5 and 9 kDa have been proven to be more efficient to remove turbidity from pond water than *Moringa oleifera* seed proteins (Bodlund *et al.* 2014). Although mustard seed has more advantages in wider distribution, abundance, and availability at low price compared with *Moringa oleifera* seed, the only application of the mustard protein for water treatment obtained from the published literature was to remove the turbidity, which limits its versatility in water treatment. Hence, our study is aimed at investigating the potential of mustard seed protein as a natural coagulant for the removal of dye from its aqueous solution.

In this study, direct black 19 (DB-19, Figure 1) was selected as a target pollutant to test the coagulation ability of white mustard seed protein (WMSP) as it is a widely

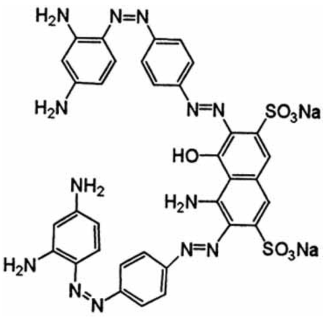


Figure 1 | Chemical r structure of DB-19 (molecular weight: 839.77).

used anionic dye, especially in some Asian countries (Shi *et al.* 2007). Meanwhile, both this dye and its reduction product have been proven to be mutagenic (Joachim *et al.* 1985). A commercial coagulant, polyaluminum chloride (PAC), that is most widely used for water treatment in China was selected to carry out the same experiment as a comparison to evaluate the coagulating performance of WMSP. The removal effects with respect to pH, settling time, temperature, coagulant dosage and influence of inorganic salts presence was investigated.

MATERIALS AND METHODS

Preparation of coagulants and dye-containing wastewater

White mustard seed (Figure 2), a traditional Chinese medicine used widely to resolve phlegm and dispel cold (vocabulary of traditional Chinese medical science), was purchased from a local pharmacy in Zhengzhou, China. The WMSP was extracted in the same way as described in our previous study (Tie *et al.* 2015). The only difference from the previous method was that the dialysis tube with a molecular weight cut-off of 3,500 Da was used in this study. The WMSP content was measured at 596 nm (UVmini-1240, Shimadzu, Japan) using bovine serum albumin as the standard (Zhou & Chen 2001). The PAC solution at the same concentration was synthesized by adding PAC into deionized water.

The DB-19 solution used in this study was prepared using the same method described in our previous study

Figure 2 | White mustard seed used in this study.

(Tie *et al.* 2015). The pH was adjusted to different values in the range of 4 to 9 using 0.1 M HCl and NaOH solution.

Jar tests

The jar tests were carried out using standard jar test equipment with six paddle gang stirrers (Model ZR4-6, Shenzhen, China). The effect of reaction time and pH on the coagulation removal of DB-19 was conducted with an initial DB-19 concentration of 30 mg/L at 25 °C in the pH range of 4–10. The influence of coagulant dosage was studied at initial DB-19 concentrations of 40, 100, and 300 mg/L at pH 8 and 25 °C, respectively. The effects of temperature and inorganic salt were conducted at an initial DB-19 concentration of 30 mg/L and pH 8.

For all the tests the equipment was programmed to mix the beakers with 200 mL of the dyeing solutions in the following procedure: rapidly mixed (120 rpm) for 1 min and followed by slow mixing (45 rpm) for 20 min (Sánchez-Martín *et al.* 2010.) The two coagulants were dosed into the beakers at the beginning of rapid mixing. Mixed matrices were collected from 2 cm below the water surface using a syringe, and the residual DB-19 concentration was determined using a UV-6000 spectrophotometer (Shanghai Metash instrument Co., Ltd., China) at the wavelength of

655 nm. The removal rate of DB-19 was calculated by the following equation:

$$R = (C_0 - C_e)/C_0 \times 100\% \quad (1)$$

where C_0 and C_e are the initial and final concentrations of DB-19 in solution (mg L^{-1}), respectively.

Characterization

Fourier transform infrared spectroscopy (FTIR, Thermo Scientific NicoletiS10, USA) and X-ray photoelectron spectroscopy (*XPS*, Thermo Scientific ESCALAB 250Xi, USA) were used to characterize WMSP, DB-19, and the reaction products between WMSP and DB-19.

RESULTS AND DISCUSSION

Effect of settling time and pH on DB-19 removal

The commercial PAC, which has been used for the removal of dyes (Shi *et al.* 2007; Huang *et al.* 2014), was used as a comparison to evaluate the coagulation ability of WMSP. Figure 3 shows the effect of settling time on DB-19 removal for both WMSP and PAC coagulants in the pH range of 4–10. Generally, the residual concentration of DB-19 decreased with increasing settling time for both of the two coagulants. The DB-19 concentrations decreased quickly within the first 30 min since the large flocs formed by both of the two coagulants during the reaction stage of slow mixing sank quickly. However, the slow sedimentation of the residual fine flocs led to a decelerating decrease of DB-19 in the following stage, and the complete sedimentation of the flocs led to invariant residual DB-19 concentrations at the settling time of 180 min.

The DB-19 removals at different pH using two coagulants are shown in Figure 4 for the two coagulants. It can be seen that the DB-19 removals decreased from 98.4 to 46.2% and 99.0 to 41.1% as the pH increased from 4 to 10 for WMSP and PAC, respectively. This indicated that a lower pH was favorable for DB-19 removal for both coagulants. Although the performance of WMSP was comparable to PAC, except at pH 4 and 5, WMSP was still very efficient for DB-19 removal.

Effect of coagulant dosage on DB-19 removal

Coagulant dosage is a very important parameter to evaluate the efficiency of the coagulation process (Boulaadjoul *et al.*

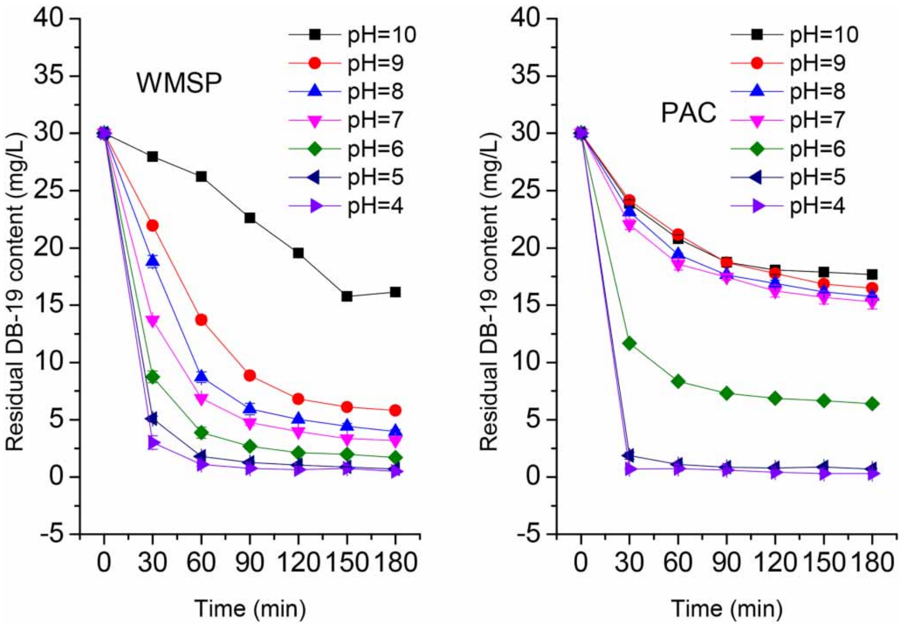


Figure 3 | Effect of settling time on DB-19 removal ($C_0 = 30$ mg/L, T = 25 °C, WMSP and PAC dosage: 5.29 mg/L).

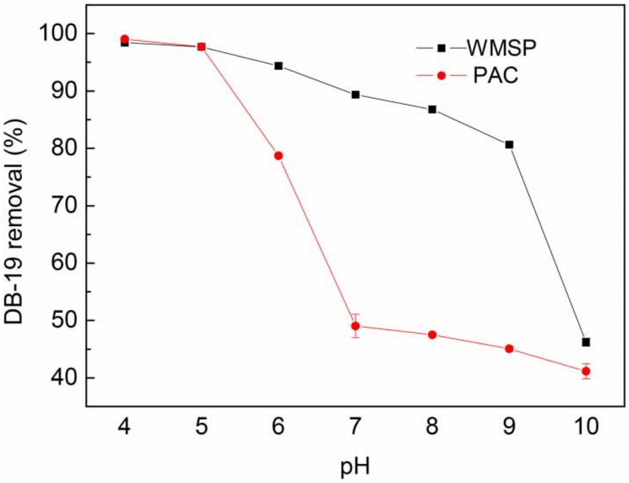


Figure 4 | Effect of pH on DB-19 removal ($C_0 = 30$ mg/L, T = 25 °C, time = 180 min).

2018). Hence, the effect of coagulant dosage on DB-19 removal was tested at DB-19 concentrations of 40, 100 and 300 mg/L because it was important that different concentrations were selected to test the significance of their impact. As shown in Figure 5, the removal efficiency of DB-19 increased significantly from 58.7 to 83.5% when the dosage of WMSP was increased from 9.0 to 18.0 mg/L for the initial DB-19 concentration of 40 mg/L. The corresponding removals for the initial DB-19 concentrations of 100 and 300 mg/L increased from 61.9 to 90.9% and from 53.3 to 89.2% as the dosage of WMSP was increased from 9.0 to 36.0 mg/L and 33.8 to 63.0 mg/L, respectively, indicating that an increasing dosage of WMSP could improve the removal of DB-19 in the tests. In the case of the same tests using PAC as the coagulant, the removal efficiency was lower at each dosage. Therefore, WMSP was shown to be more efficient for DB-19 removal than PAC in the experiment.

Effect of temperature on DB-19 removal

Figure 6 shows the effect of temperature on DB-19 removal in the range of 10–45 °C. It can be seen that the removal rate varied at 31.7–43.7% for PAC and 70.0–83.2% for WMSP, respectively. At each temperature set for the experiment, WMSP performed better than PAC for DB-19 removal. The optimal temperature for DB-19 removal by both of the two coagulants was 25 °C, and the corresponding removal rates were 43.7 and 83.2% for PAC and WMSP, respectively.

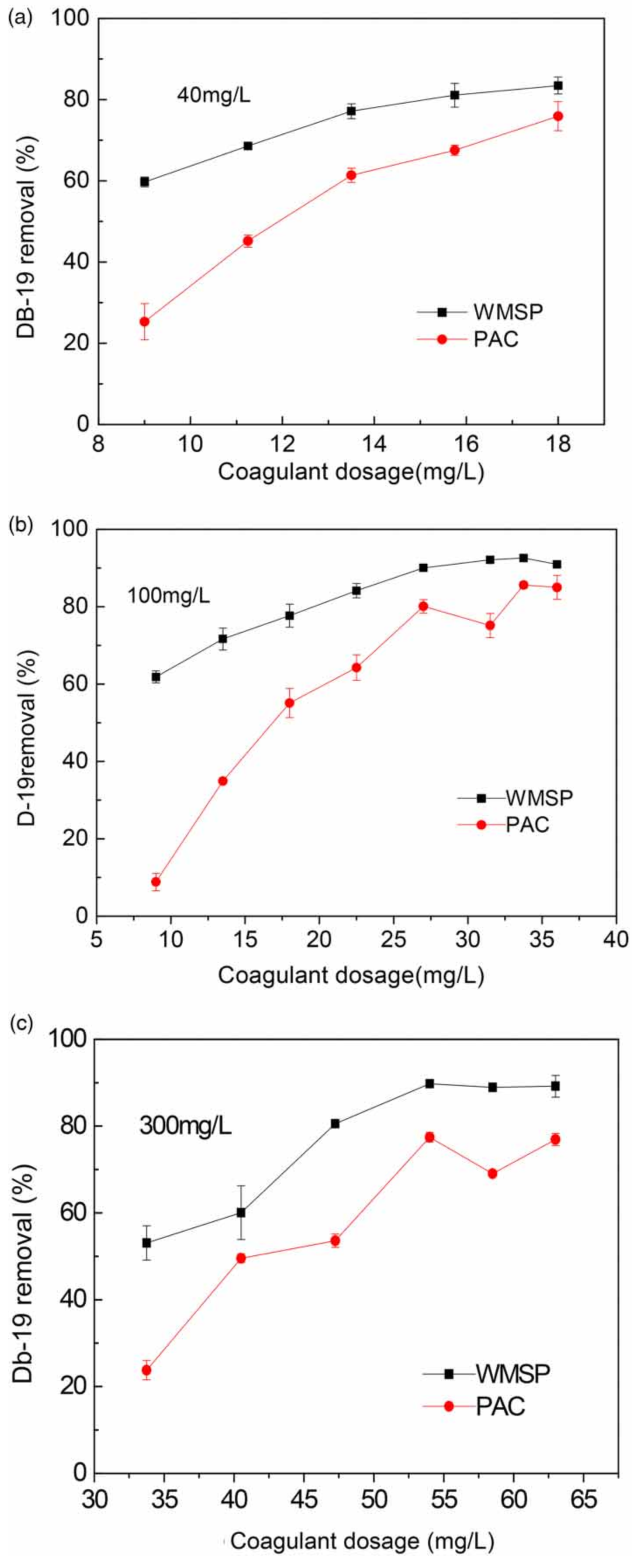


Figure 5 | Effect of coagulant dosage on DB-19 removal (pH = 8, T = 25 °C, settling time = 120 min).

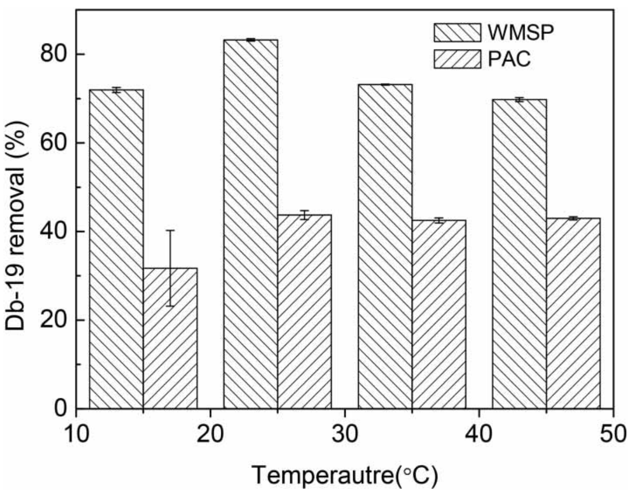


Figure 6 | Effect of temperature on DB-19 removal ($C_0 = 30$ mg/L, pH = 8, settling time = 120 min).

The test results indicated that WMSP was more efficient than PAC at all selected temperatures.

Effect of the presence of inorganic salt on DB-19 removal

Sodium sulfate is widely adopted to improve dyeing performance and fixation property by enhancing the dye molecules transfer from the solution to cotton fibers when direct dyes are used (Teixeira *et al.* 2012). Hence, the effect of Na_2SO_4 on DB-19 removal was investigated. Figure 7 shows that, overall, Na_2SO_4 weakened the DB-19 removal for both coagulants, whereas WMSP still outperformed PAC in the presence of Na_2SO_4.

Mechanism of DB-19 removal by WMSP

The effect of pH on the flocculation is critical to explore the coagulation mechanism (Teixeira *et al.* 2012). Figure 8 shows the effect of pH on WMSP content. The lowest WMSP content occurred at pH 9.0, indicating the isoelectric point of WMSP was around pH 9.0 due to the fact that protein as an amphoteric compound has the least solubility at the isoelectric point (Zhao *et al.* 2017). Hence, WMSP was positively charged by adsorbing H^+ on its amino-groups in the pH range of –9 set for the experiment.

Figure 9(a) shows the spectrum of WMSP, DB-19 and their flocs formed by WMSP and DB-19. The band at 2,960 cm^{-1} was ascribed to the CH_3 asymmetrical stretching (Fournier *et al.* 2008). The bands at 1,654.6, 1,540.8 and 1,241.9 cm^{-1} were assigned to the C = O stretching (Amide I), the CN stretching (Amide II) and the NH bending (Amide III), respectively (Kong & Yu 2007). Figure 9(b) shows the spectrum of DB-19. The bands at 1,616.9 and 1,483 cm^{-1} were ascribed to the C = C stretching of the benzenoid ring (Wang *et al.* 2007; Ge *et al.* 2012). The band at 1,045.2 cm^{-1} in the dye was ascribed to SO_3^- stretching (Abd-alredha *et al.* 2012). The band at

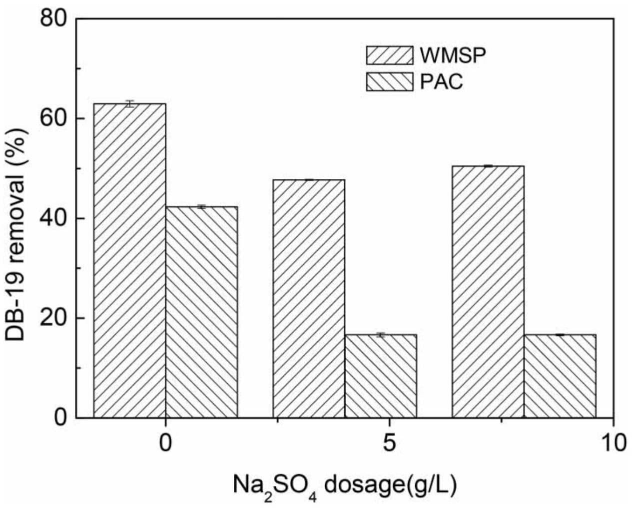


Figure 7 | Effect of inorganic salt on DB-19 removal by WMSP and PAC on DB-19 removal ($C_0 = 30$ mg/L, pH = 8, settling time = 2 h).

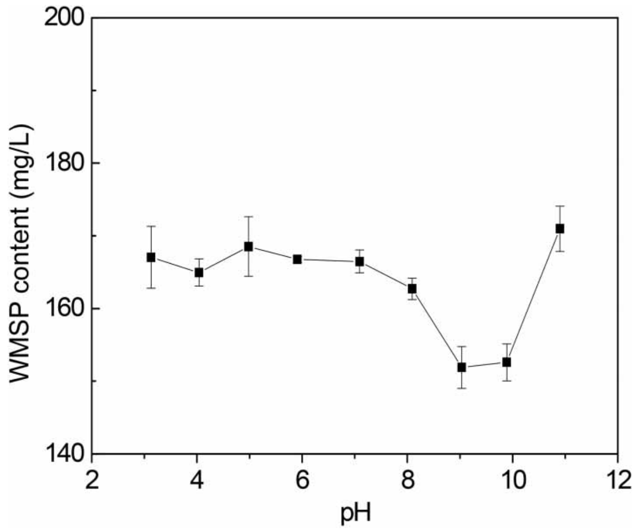


Figure 8 | WMSP content variety as a function of pH.

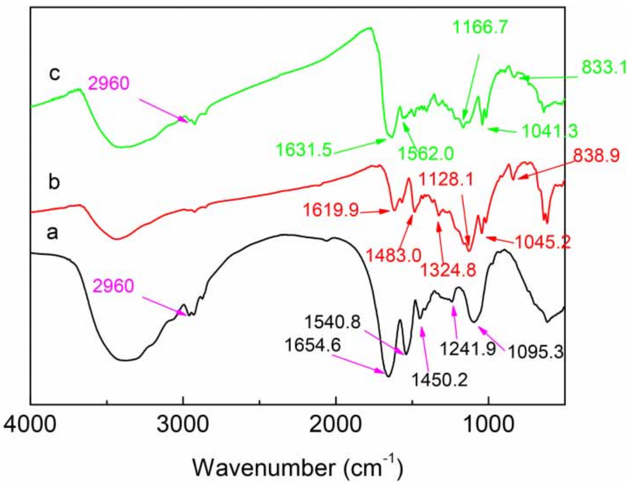
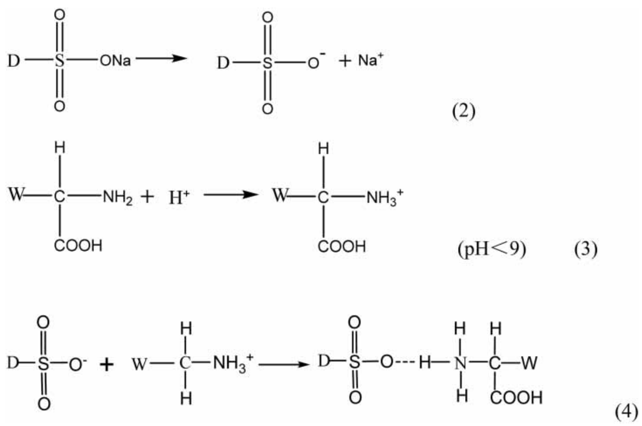


Figure 9 | FTIR of WMSP (a), DB-19 (b), DB-19/WMSP flocs (c).

838.9 cm^{-1} belonged to the C_6H_4 bending (Khan *et al.* 2013). Figure 9(c) shows the spectrum formed by DB-19/WMSP flocs. The bands of WMSP at 1,654.6 and 1,540.8 cm^{-1} shifted to 1,631.5 and 1,562.0 cm^{-1}, respectively. The bands of DB-19 at 838.9 cm^{-1} shifted to 833.1 cm^{-1}, which resulted from the electrostatic attraction between the negatively charged sulfo groups of DB-19 and the protonated amino groups of the WMSP.

To further reveal the removal of DB-19 by WMSP, XPS was employed to monitor the elemental composition and chemical state of DB-19, WMSP and their flocs formed by WMSP and DB-19, respectively. As shown in Figure 10(a), DB-19, WMSP and their flocs formed by WMSP and DB-19 consisted of the same elements of C, O, N and S. Moreover, there was an Na 1 s peak around 1,068 eV in DB-19, which was assigned to Na^+. Through the linear least-squares fit program by using Gauss–Lorentzian peak shapes (Yamashita & Hayes 2006), it was found that there were two chemical states of S 2p in DB-19 ($2p_{3/2}$ 169.3 and 167.8 eV), which was attributed to -S(=O)$_2$-O-Na and -S(=O)$_2$-O-H (Figure 10(b)). Typically, there were also two chemical states of S 2p in WMSP, namely 2p3/2 of 167.6 and 163.5 eV, assigned to -S-S- and -SH, respectively (Figure 10(c)). After DB-19 reacted with WMSP, the chemical state of S 2p of -S(=O)$_2$-O-Na disappeared and a new chemical state $S2p_{3/2}$ (168.7 eV) appeared. This was due to the formation of DB-19/WMSP flocs. Moreover, the binding energy of $S2p_{3/2}$ of -S(=O)$_2$-O-H in DB-19 decreased to 167.3 eV, which was caused by the strong hydrogen bonding between -S(=O)$_2$-O-H of DB-19 and hydrogen bonding donors (e.g. -NH_2, -COOH) (Figure 10(d)). It should be noted that -S-S- as the internal chemical information of the WMSP/DB-19 flocs could not be detected due to the limitation of XPS. This result is in accordance with the research of Iwahashi *et al.* (2009) and Du *et al.* (2015), who have undertaken in-depth studies of the difference between the surface and interior of materials. According to the analysis of isoelectric point of WMSP, FT-IR and XPS results, it is concluded that adsorption and charge neutralization was the main mechanism for the coagulation reaction between WMSP and DB-19. Ndabigengesere *et al.* (1995) reported that adsorption and charge neutralization was the mechanism for the removal of turbidity using *Moringa oleifera* seed protein with isoelectric points between pH 10 and 11 as the coagulant. The reaction between WMSP and DB-19 can be described by the following equations:



where D and W denote DB-19 and WMSP, respectively.

The decrease of residual DB-19 content with descending pH shown in Figure 3 can be explained by the mechanism mentioned above. The adsorption and charge neutralization between WMSP and DB-19 was weakened, resulting in higher residual DB-19 content since WMSP molecular was negatively charged at pH 10 higher than its isoelectric point of pH 9. However, the reaction was reinforced by the increase of positive charge of WMSP with decreasing

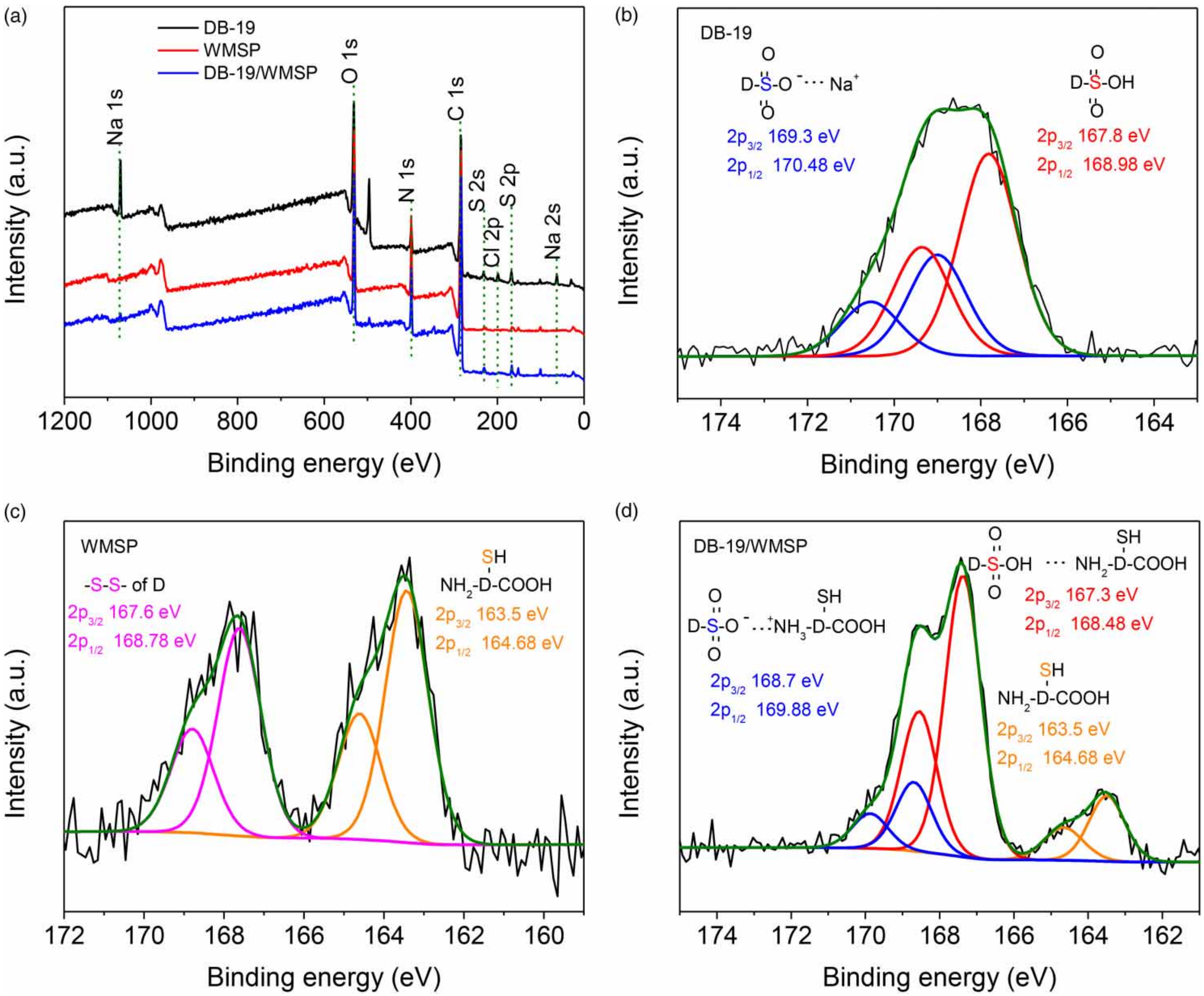


Figure 10 | XPS survey spectra of wide scan of DB-19, WMSP and DB-19/WMSP flocs (a); high magnification of S 2p of DB-19 (b); high magnification of S 2p of WMSP (c); high magnification of S 2p of DB-19/WMSP flocs (d), where D and W represent DB-19 and WMSP, respectively.

pH below its isoelectric point to create lower DB-19 residual.

CONCLUSIONS

This study describes an attempt of removal of the anionic dye DB-19 from water using proteins extracted from white mustard seed as a natural coagulant. The results indicate that the coagulation efficiency of WMSP was better than PAC at the same dosage for all other experiments except at pH 4 and 5. The main mechanism of the removal of DB-19 by WMSP could be adsorption and charge neutralization.

To our knowledge, it is the first report on removal of an anionic dye using WMSP as a natural coagulant, and the results showed that WMSP had excellent coagulation ability to remove DB-19.

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