

Coagulation performance of cucurbit[8]uril for the removal of azo dyes: effect of solution chemistry and coagulant dose

Wendong Wang, Zhiwen Chen, Kun Wu, Zongkuan Liu, Shengjiong Yang, Qin Yang and Mawuli Dzakpasu

ABSTRACT

Dye wastewater has attracted significant attention because of its wide pH range and high content of color. In this work, the coagulation performances of cucurbit[8]uril for the removal of color from acid red 1 (AR1), orange II (OII), and Congo red (CR) dye wastewaters were investigated. Experimental results showed that color removal rates of greater than 95% for AR1, OII and CR were achieved at pH 6.0, when the dosage of cucurbit[8]uril was 1.51, 3.01 and 0.38 mmol·L⁻¹, respectively. Under identical conditions, the color removal efficiencies of AR1 and CR were higher than OII, due to the larger molecular weights and more active hydroxyl and amino groups. Moreover, steady increases in AR1, OII and CR removal rates were recorded with increasing ionic strength. Such increases may be related to the reduction in thickness of the surface solvent membrane surrounding the dye colloids at high ionic strengths. Furthermore, Fourier transform infrared spectra demonstrated that no new bonds or functional groups were formed during coagulation, which indicates that the removal of AR1, OII and CR was primarily a physical process. The hydrogen bonds and inclusion complexes formed between cucurbit[8]uril and AR1, OII and CR contributed to the removal of color in coagulation predominantly.

Key words | coagulation, color removal, cucurbit[8]uril, dye wastewater, ionic strength

Wendong Wang (corresponding author)
Zongkuan Liu
School of Human Settlements and Civil
Engineering,
Xi'an Jiaotong University,
Xi'an 710049,
China
E-mail: wdwang@xjtu.edu.cn

Zhiwen Chen
Kun Wu
Shengjiong Yang
Mawuli Dzakpasu
Department of Environmental and Municipal
Engineering,
Xi'an University of Architecture and Technology,
Xi'an 710055,
China

Qin Yang
School of Science,
Xi'an University of Architecture and Technology,
Xi'an 710055,
China

INTRODUCTION

Dye wastewaters are produced by many industries, such as clothing, printing, and textiles. Effluents discharged by these industries usually have high contents of organic compounds and salts (Zhu *et al.* 2015). Not only does the discharge of dye wastewater create aesthetic problems, but also it upsets the biological processes in natural water bodies as the penetration of sunlight is inhibited (Wawrzki-wicz *et al.* 2015). Furthermore, many types of dyes show high toxicities to aquatic communities. Among them, azo dyes, which have nitrogen–nitrogen double bonds in their structure, are the largest class of organic dyes. These azo dyes are also the most difficult to degrade due to their complicated aromatic structures and poor biodegradability (Merzouk *et al.* 2011). Consequently, decolorization treatment of azo dye wastewater has attracted considerable attention in recent years.

Technologies such as coagulation, adsorption, chemical oxidation, and membrane processes have been widely used

in the treatment of azo dye wastewaters (Merzouk *et al.* 2011; Nguyen & Juang 2013; Han *et al.* 2016; Cao *et al.* 2017). Among these methods, coagulation is widely used prior to biological treatment units. During the above process, hydrophobic dye molecules can be coagulated by the addition of chemicals. In contrast, decolorization of hydrophilic dyes such as those containing sulfonic acid groups becomes difficult to achieve (Kim *et al.* 2004). Regarding the type of coagulant, although inorganic salts can be used for the removal of azo dyes, their effectiveness is strongly pH-dependent (Vakili *et al.* 2014), which restricts the application of these coagulants.

Cucurbituril[n] (CB[n]) consists of macrocyclic molecules made of glycoluril monomers linked by methylene bridges, where 'n' is the number of glycoluril units. With the possession of -OH and -NH₂ groups, it can form stable clathrate compounds with other organic matters through van der Waals forces, hydrophobic interaction, electrostatic

force and hydrogen bonding (Wang *et al.* 2016). Furthermore, CB[n] has a relatively stable chemical structure and low toxicity to aquatic communities (Xiao *et al.* 2013). Therefore, its application in water treatment has been burgeoning in recent years. CB[6] was first used as an adsorbent in the treatment of reactive orange 96, reactive red 198, and reactive red 120 dye wastewaters and exhibited a high adsorption efficiency (Karcher *et al.* 2001). Recently, Yang *et al.* (2012) determined that magnetic CB[n] could adsorb HA (humic acid) effectively from micro-polluted water.

Nevertheless, dye wastewater often has a high ionic strength (as sodium salts are added to dyebaths), which makes CB[6] unlikely to perform well as an adsorbent because of the damage to its structure by the notable increase in its solubility. Buschmann *et al.* (1994) used CB[6], which was fixed on silica through physical precipitation. However, adhesion forces could not prevent its dissolution. Efforts to fix CB[n] on a support material have been made in other works (Xiao *et al.* 2013), but to date, there are no reports regarding a successful attempt for azo dye adsorption. It should be noted that although the solubility of cucurbiturils in high ionic strength solutions is high, it decreases notably when the dye are adsorbed on it (Karcher *et al.* 1999). Moreover, most of the azo dyes have large molecular weights and show typical colloidal characteristics. Considering its good adsorption performance, CB[n] may be used as an alternative coagulant for the enhanced removal of color from azo dye wastewater. However, the coagulation performance of CB[n] has rarely been reported in the literature.

The primary objective of this work, therefore, is to investigate (i) the coagulation performance of CB[8] in the removal of color from azo dye wastewaters containing acid red 1 (AR1), orange II (OII), and Congo red (CR), respectively, with sulfonic acid groups in their structure and (ii) the effects of pH and ionic strength on the coagulation process. The mechanisms of coagulation using CB[8] are discussed referencing the experimental results.

MATERIALS AND METHODS

Synthetic test water

All chemicals were purchased from Sigma Aldrich (USA). The characteristics of three dyes, AR1 (2,7-naphthalenedisulfonic acid, 5-(acetylamino)-4-hydroxy-3-(2-phenyldiazenyl)-, disodium salt), OII (tetrasodium salt of 4-amino-5-hydroxy-3,6-bis((4-((2-(sulfooxy) ethyl) sulfonyl)

phenyl)azo)-2,7-naphthalenedisulfonic acid) and CR (sodium salt of 3,3'-([1,1'-biphenyl]-4,4'-diyl) bis (4-aminonaphthalene-1-sulfonic acid)), are listed in Table 1. Synthetic wastewater was prepared by adding a measured amount of AR1, OII, or CR into distilled water to maintain an initial concentration of 50 mg·L⁻¹. The alkalinity of the synthetic wastewater, adjusted using NaHCO₃, was 1.2 mmol·L⁻¹. The maximum absorption wavelength and absorbance of the synthetic wastewater were determined to be 531 nm and 1.90 for AR1, 484 nm and 2.89 for OII, and 495 nm and 1.32 for CR, respectively.

Preparation of coagulant usage solution

The coagulant (CB[8]) was synthesized and purified following the method suggested by Bi *et al.* (2007). To create a CB[8] usage solution, 2.5 g of CB[8] was mixed with 50 mL deionized water. The dissolving process was performed under a supersonic wave environment for 30 min. The mixture was centrifuged at 5,000 rpm for 20 min, and then the residual solids were removed. The concentration of CB[8] dissolved in solution was determined to be 4.2 mmol·L⁻¹, based on the amounts of total added and the residual CB[8].

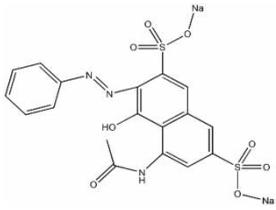
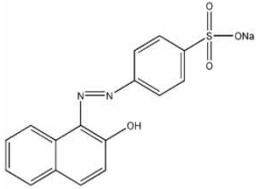
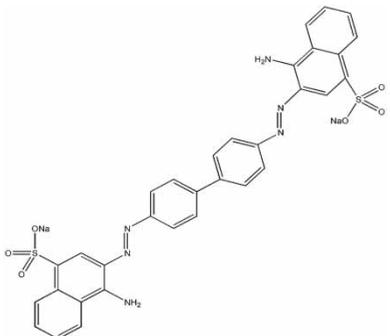
Coagulation tests

The synthetic wastewater was coagulated using a jar tester (MY3000-6, Meiyu Water Industry Technology Development Co. Ltd, China) with the CB[8] usage solution. The coagulation procedure, which was obtained based on the removal efficiency of azo dyes, involved rapid mixing at 250 rpm for 1.0 min, followed by 15.0 min of flocculation at 75 rpm, and 30.0 min settling. A 20 mL water sample was taken from 2.0 cm below the water surface.

Effects of coagulant dosage, pH, and ionic strength on the removal of azo dyes

The effects of coagulant dosage, pH, and ionic strength on the coagulation performance of CB[8] were investigated using single-factor testing method (Table 2). Solution pH was adjusted using 0.1 mol·L⁻¹ HCl and 0.1 mol·L⁻¹ NaOH. Except for the experiment investigating the effects of pH on hydrophilic dye removal, the pH of the synthetic wastewater was controlled at 6.0. The effects of ionic strength on the removal of AR1, OII, and CR were examined by adding pre-determined amounts of stock solutions of 1.0 mol·L⁻¹ NaCl to the synthetic wastewater. Water temperature was controlled at 15 °C (the average temperature

Table 1 | The structure, molecular weight, maximum absorbance, and maximum wavelength of the selected azo dyes

Name	Molecular weight (Dalton)	Molecular structure	Wavelength (nm)	Absorbance
AR1	509.4		531	1.90
OII	350.3		484	2.89
CR	696.6		495	1.32

of dye wastewaters in winter in China) throughout the experiment.

Water quality and coagulant structure analysis

The color removal rate ($R\%$) of AR1, OII, and CR was calculated according to Equation (1). Both A_0 and A , which showed a linear relationship with the concentration of dyes, were determined with a UV-visible spectrometer (UV-1650PC, Shimadzu, Japan) (Shi *et al.* 2007). To avoid

the interference of solution pH, the pH of water samples was adjusted to about 7.0 using $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl and $0.1 \text{ mol}\cdot\text{L}^{-1}$ NaOH before conducting determination. The zeta potential (ζ) of the coagulated water was measured using a zeta meter (Nano-Z, Malvern, UK). The solution pH was determined using a pH meter (Model 828, Thermo Electron Corporation, USA).

$$R(\%) = (1 - A/A_0) \times 100 \quad (1)$$

Table 2 | Synthetic wastewater quality, coagulant dosage, and corresponding levels selected in single-factor experiments

Factors	Levels selected for pH, ionic strength, and CB[8] dosage ($\text{mmol}\cdot\text{L}^{-1}$, except for pH)									T^* ($^{\circ}\text{C}$)	pH	Dye content ($\text{mg}\cdot\text{L}^{-1}$)	Turbidity (NTU)	Alkalinity ($\text{mmol}\cdot\text{L}^{-1}$)	Ionic strength ($\text{mmol}\cdot\text{L}^{-1}$)
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)						
pH	2.0	4.0	5.0	6.0	7.0	8.0	9.0	–	–	15	var.**	50.0	4.8	1.2	1.20
Ionic strength	1.20	2.91	9.75	18.3	35.4	52.5	86.7	–	–	15	6.0	50.0	4.8	1.2	var.
CB[8] dosage	0.15	0.23	0.30	0.38	0.75	1.51	2.26	3.01	3.77	15	6.0	50.0	4.8	1.2	1.20

*Water temperature; **the variable parameter.

where A_0 and A are the absorbance of the dyeing wastewater before coagulation and after 30 min of settling at the maximum wavelength of the corresponding hydrophilic azo dye.

To observe the structural characteristics of the CB[8] and the flocs formed after coagulation, infrared analysis was conducted using an infrared spectrometer (IFS 55, Bruker, Germany) in transmission mode (200 scans collected at 2 cm^{-1} resolution in the $4,000\text{--}400\text{ cm}^{-1}$ range). The primary Fourier transform infrared (FT-IR) bands were assigned according to the method described by Gu *et al.* (2000).

RESULTS AND DISCUSSION

Effects of coagulant dosage on the removal of AR1, OII, and CR

The experiments were conducted at pH 6.0 and $15\text{ }^\circ\text{C}$. Similar to HAs, AR1 showed typical colloidal characteristics (Merzouk *et al.* 2011). As the CB[8] dosage increased, the decolorization efficiency of AR1 dye wastewater increased sharply (Figure 1). At the coagulant dosage of $0.75\text{ mmol}\cdot\text{L}^{-1}$, its color removal rate was above 90%. However, it was only when the color removal rate was above 95%, corresponding to a CB[8] dosage of $1.51\text{ mmol}\cdot\text{L}^{-1}$, could the color removal be sufficiently visible to the naked eye. With increasing CB[8] dosage, the zeta potential of the coagulated system rose steadily (Figure 1). This phenomenon may be primarily related to the hydrolysis process of CB[8] (Mock & Shih 1986). The zeta

potential of the coagulation system was close to zero when the CB[8] dosage was $1.51\text{ mmol}\cdot\text{L}^{-1}$. However, the color removal rate of AR1 was not the optimum at this point. It is theorized that if charge neutralization is the only path for coagulation, the zeta potential should be in excellent correlation with the coagulation dosage and optimal efficiency is achieved when zeta potential is close to zero (Pefferkorn 2006). This suggested that the removal of AR1 was not entirely dependent on the charge neutralization function of CB[8]. Other factors, such as the adsorption-bridge building effect, may also contribute to the removal of AR1.

OII is also a water-soluble acidic dye (Ramavandi *et al.* 2014). Because the structure has a lower number of active groups, such as $-\text{OH}$ and $-\text{NH}_2$ that may interact with CB[8], the decolorization efficiency in the coagulation process might be affected. As shown in Figure 1, the color removal rate of OII was 69.5% at the coagulant dosage of $0.75\text{ mmol}\cdot\text{L}^{-1}$. From the macro view, the color of the coagulation effluent did not vary significantly from the original water. To achieve a removal rate of above 95%, CB[8] dosage was increased to approximately $2.26\text{ mmol}\cdot\text{L}^{-1}$, which was higher than the minimum dosage for AR1 under the same condition. With increasing CB[8] dosage, the zeta potential in the OII coagulation system also rose steadily (Figure 1). Similar to AR1 wastewater, OII wastewater did not achieve optimal coagulation efficiency under the condition where zeta potential was close to neutral. Nonetheless, it still showed a slow upward trend with increasing dosages of CB[8].

Compared with AR1 and OII, CR has the largest molecular weight (Table 1). Its molecule also contains the largest number of active groups. Under the same water quality conditions, the decolorization efficiency of CR dye wastewater was the best (Figure 1). The coagulation test results showed a favorable decolorization efficiency (94%) at a coagulant dosage of $0.15\text{ mmol}\cdot\text{L}^{-1}$ (Figure 1). In the case of the coagulant dosage of $0.38\text{ mmol}\cdot\text{L}^{-1}$, the color removal rate reached 98%, and the zeta potential of the coagulation system was -4.83 mV . This finding indicated that when applying CB[8] as a coagulant, similar coagulation mechanisms existed for AR1, OII and CR dyes. In addition to charge neutralization, other processes may have also contributed to the decolorization of the selected hydrophilic azo dye wastewaters.

Effects of solution pH on the removal of AR1, OII, and CR in coagulation

For AR1 synthetic wastewater, a minimal impact of pH on the decolorization efficiency was observed at pH 2.0–8.0,

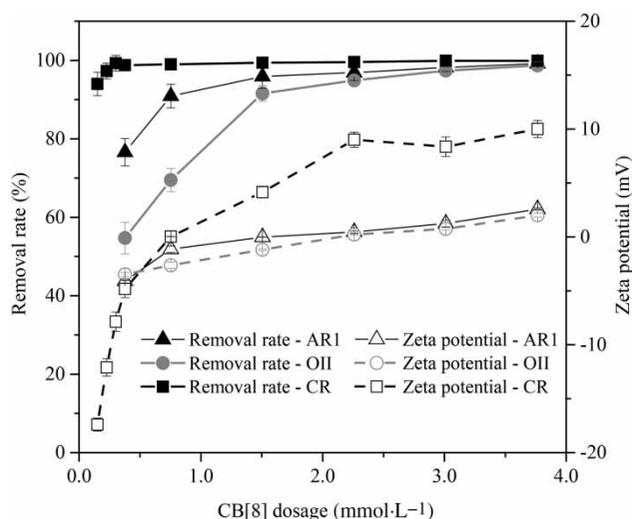


Figure 1 | Effects of CB[8] dosage on the removal of color from AR1, OII, and CR dyeing wastewaters at pH 6.0 (dye concentration = $50\text{ mg}\cdot\text{L}^{-1}$). Error bars represent standard error of three replicates.

whereby the color removal rate remained approximately 91% at the coagulant dosage of $0.75 \text{ mmol}\cdot\text{L}^{-1}$ (Figure 2). Meanwhile, the zeta potential of the coagulation system was positive under acidic conditions and decreased significantly with increasing pH. The decreasing charges on the AR1 molecule likely contributed to its high removal rate at pH levels below 8.0. At $\text{pH} > 8.0$, the zeta potential became negative and continually decreased with increasing pH. Because the increased electrostatic repulsion inhibited the aggregation of colloidal particles (Merzouk *et al.* 2011), the color removal rate of AR1 declined significantly to 85% at $\text{pH} 9.0$.

It should be noted that although the zeta potential of AR1 had a greater amplitude variation under acidic conditions, decreasing from 15.5 mV at $\text{pH} 2.0$ to approximately 0.0 mV at $\text{pH} 7.0$, the decolorization efficiency was not noticeably affected (Figure 2). In contrast, when the pH was increased to 9.0, the zeta potential of AR1 was further reduced to -7.23 mV . Although the absolute variation was far below 15.5 mV, the decolorization efficiency of AR1 reduced by 6% after coagulation. A similar phenomenon was observed by Chen *et al.* (2010) where polyferric chloride–polyamine dual-coagulants were used in the coagulation of synthetic reactive red wastewater. This finding further indicated that except for charge neutralization, other factors, such as adsorption-bridge building effects, may have contributed to the flocculation of AR1.

Compared with AR1, OII and CR displayed similar removal properties with variations in pH. At $\text{pH} 4.0$, the zeta potential of OII and CR approached neutral,

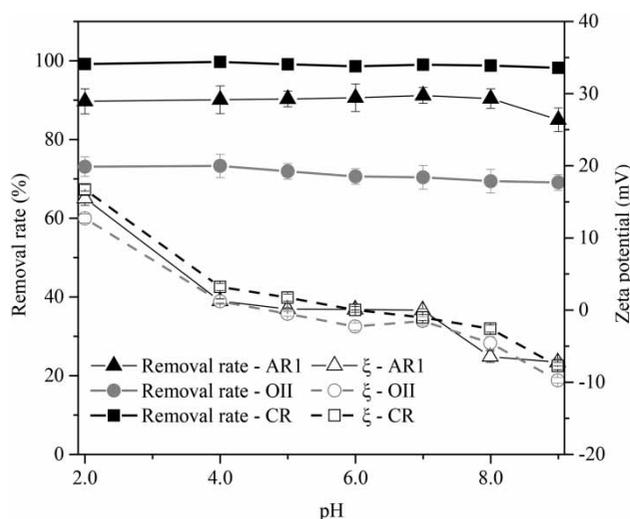


Figure 2 | Effects of pH on the removal of color from AR1, OII, and CR dyeing wastewaters (dye concentration = $50 \text{ mg}\cdot\text{L}^{-1}$, CB[8] dosage = $0.75 \text{ mmol}\cdot\text{L}^{-1}$). Error bars represent standard error of three replicates.

corresponding to maximum removal levels of 73.3% and 99%, respectively (Figure 2). Conversely, at pH levels below and above 4.0, the increased absolute value of the zeta potential inhibited their removal by coagulation. Such a phenomenon demonstrated that charge neutralization did contribute to the removal of OII and CR in coagulation. However, the variations in decolorization efficiency of OII and CR did not correlate with the reduction of the zeta potential (Figure 2). Nonetheless, although the zeta potentials of CR and AR1 dye wastewaters were similar, the color removal rate of CR was much higher than that of AR1, which was likely due to differences in their molecular structures.

Merzouk *et al.* (2011) applied alum for coagulation of a red dye synthetic wastewater and determined that the color removal efficiency was significantly affected by pH. Effective removal of color in the red dye wastewater was achieved at $\text{pH} 4.0\text{--}6.1$. Nevertheless, even at $\text{pH} 6.1$, only 73% of the color was removed at the alum dosage of $50 \text{ mg}\cdot\text{L}^{-1}$. By changing chemical coagulation to electrocoagulation (wastewater conductivity = $2.4 \text{ mS}\cdot\text{cm}^{-1}$, residence time = 14 min), the color removal efficiency increased to 82% under the same pH and coagulant dosage (Merzouk *et al.* 2011). Considering that most actual azo dye wastewaters present a certain acidity or alkalinity, it is necessary to strictly control the pH of the wastewater when conventional coagulants, such as alum, are used. By contrast, CB[8] has a broad optimal pH range of 2.0–9.0 for the removal of AR1 in coagulation, 2.0–8.0 for OII, and 2.0–9.0 for CR (Figure 2). Thus, color removal efficiencies could be significantly improved (above 98% for AR1, OII, and OII) without pH adjustment, enabling CB[8] to be used as an alternative choice for the coagulation of dye wastewater.

Effects of ionic strength on color removal from AR1, OII, and CR in coagulation

In addition to acids and bases, salts, including sodium carbonate, sodium bicarbonate, sodium polyphosphate, sodium chloride, sodium sulfate and sodium dithionate, are usually added in the printing process (Al-Degs *et al.* 2008). Most of these salts are finally transferred to the aqueous phase, causing dyeing wastewaters to exhibit strong ionic strengths. Variations in ionic strength may affect the speciation of dyes and the hydrolysis of CB[8], thus affecting the removal of color in coagulation. In this paper, NaCl was used to adjust the ionic strength of the AR1, OII and CR synthetic wastewaters. With increasing ionic strength, the zeta potential of the coagulation system showed a notable

upward trend (Figure 3). When the ionic strength increased from 1.20 to 86.7 mmol·L⁻¹, the zeta potential of AR1, OII and CR increased from -1.2, -1.9, and 0.03 mV to 13.2, 12.8, and 15.2 mV, respectively.

Based on the above discussion, it could be concluded that the increase of absolute zeta potential inhibits the coagulation process of AR1, OII and CR. With the introduction of NaCl to the synthetic wastewater, the zeta potential of AR1, OII and CR increased notably (Figure 3). However, the color removal rates of the corresponding wastewaters did not decrease but increased to variable degrees. Additionally, the stronger the ionic strength, the better the decolorization efficiencies. *Esmaeli et al. (2013)* also demonstrated that the presence of salts increased the decolorization efficiency of dye wastewater. This finding illustrated that charge neutralization was likely not the major reason for the destabilization of AR1, OII and CR. The effects of ionic strength on the coagulation process may be related to variations in the physicochemical characteristics of the colloids.

At a coagulant dosage of 0.75 mmol·L⁻¹, as NaCl was introduced, the decolorization rate of AR1 increased slowly. When the ionic strength was 18.3 mmol·L⁻¹, the removal rate of color was 93.1%, which increased to 95.6% as the ionic strength increased to 86.7 mmol·L⁻¹ (Figure 3). Although only 2.5% improvement in AR1 removal was achieved, the treated water appeared visibly cleaner to the naked eye. Conversely, there was no apparent variation in the color removal rate of CR within the studied

ionic strengths, which was possibly due to the larger number of active groups on its molecule. Compared with AR1 and CR, ionic strength notably improved the decolorization rate of OII in coagulation. When the ionic strength was 18.3 mmol·L⁻¹, the color removal rate of OII was 83.1%, increasing to 90.3% when the ionic strength of the synthetic wastewater was 86.7 mmol·L⁻¹ (Figure 3).

Mechanism of AR1, OII and CR coagulation by CB[8]

As shown in Figure 1, the zeta potentials of AR1, OII and CR increased with the addition of the coagulant. This increase indicated that CB[8] had a positive charge that may be produced by the protonation of nitrogen and oxygen with the formation of =N-H⁺ and =O-H⁺ under neutral and acidic conditions (*Mock & Shih 1986*). Accordingly, electrical double-layer compression or charge neutralization might contribute to the removal of negatively charged AR1, OII and CR in coagulation. The achievement of optimal coagulation efficiencies at zeta potentials close to zero for AR1, OII and CR in the coagulation system confirms this. Unlike coagulants with small molecules, CB[8] has a large three-dimensional cage-like structure. Therefore, its impact on the zeta potential of the dye particles is considered to be mainly charge neutralization but not electrical double-layer compression (*Huang et al. 2014*).

Furthermore, there are several phenolic hydroxyl and amino groups on the molecules of AR1, OII and CR, which might form hydrogen bonds (a typical type of 'bridge') with the O and N existing on the molecular CB[8] (Figure 4). Furthermore, inclusion complexes may form between CB[8] and selected dyes, providing another type of 'bridge' in the coagulation process (*Karcher et al. 1999*). Under the adsorption-bridge building effect, destabilization and aggregation of dye molecules occurred with the formation of dye-CB-dye flocs (Figure 4). Moreover, part of the dyes might also be removed by the porous flocs through sweep flocculation (*Duan & Gregory 2003*), which contributed an extra 20–40% of HA removal when CB[8] was not used as an adsorbent but a coagulant under the same condition (*Wang et al. 2016*). Accordingly, CB[8] showed a strong capacity for the removal of hydrophilic AR1, OII and CR dyes in coagulation.

The FT-IR spectra of AR1, OII, and CR flocs which were formed in coagulation exhibited no new peaks, which indicated that the coagulation of selected hydrophilic azo dyes by CB[8] is mainly a physical process (Figure 5). The bands at 3,430 cm⁻¹ and 1,620 cm⁻¹, which correspond to O-H and N-H stretching, respectively, became stronger,

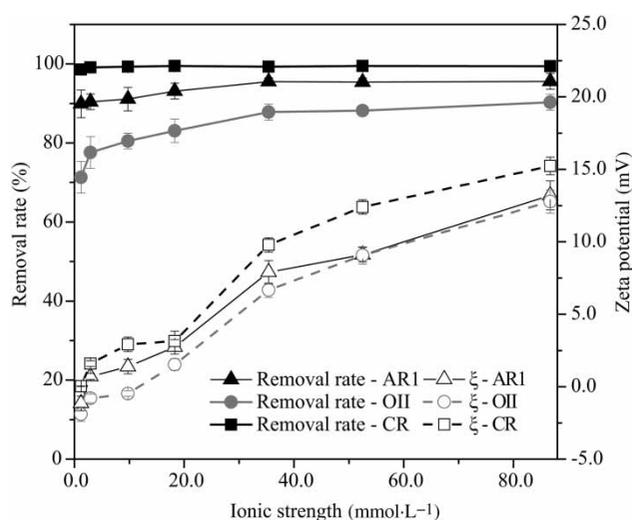


Figure 3 | Effects of ionic strength on the removal of color from AR1, OII, and CR dyeing wastewaters (pH = 6.0, dye concentration = 50 mg·L⁻¹, CB[8] dosage = 0.75 mmol·L⁻¹). Error bars represent standard error of three replicates.

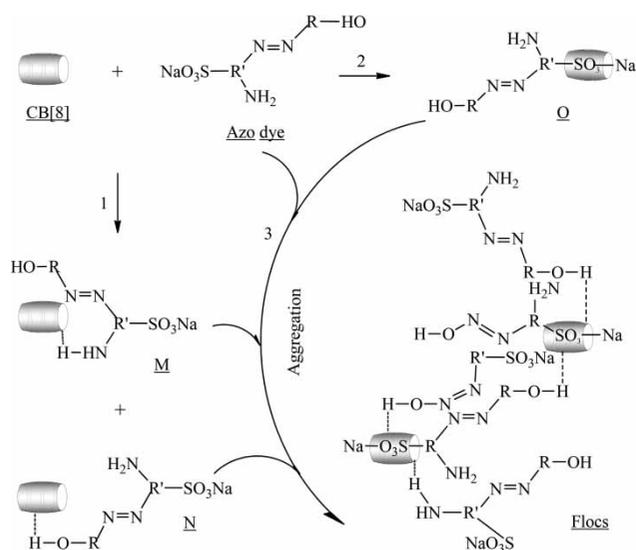


Figure 4 | Possible coagulation mechanism of CB[8] for the removal of AR1, OII, and CR. The lines at both ends of the schematic structure of CB[8] represent the adsorption points contributed by oxygen; two dash lines in the middle represent adsorption points contributed by nitrogen. R and R' in the dye molecule represent aromatic structures.

indicating that the oxygen and nitrogen in CB[8] formed hydrogen bonds with the phenolic hydroxyl (-OH) and -NH₂ groups on AR1, OII, and CR molecules after coagulation. Under basic conditions, the amount of protonated -OH was relatively low, thus inhibiting the adsorption of dyes on CB[8], which is inconsistent with the results presented in Figure 2.

It should be noted that by applying charge neutralization and adsorption-bridge building theory, it is still difficult to explain the enhanced decolorization efficiency of the synthetic wastewater with increasing ionic strength. Such enhancement may be related to the influence of ionic strength on the physicochemical properties of the reaction system. Karcher *et al.* (1999) found that the solubility of CB[6] in the aqueous phase increased with the addition of sodium salts, which may be explained by the fact that the thickness of the CB[6] hydration shell was reduced with the addition of salts. In addition to electrostatic repulsion, steric hindrance caused by the existence of the hydration shell also facilitated the stability of hydrophilic colloids (Edzwald & Haarhoff 2001). Similarly, at high ionic strengths, the thickness of the hydration shell would also be reduced to become conducive for the destabilization of AR1, OII, and CR.

Based on the above analysis, it could be concluded that, in addition to CB[8] dosage, pH, and ionic strength, the quantities of active groups and dye molecular size may also affect the coagulation performance of CB[8]. Of the

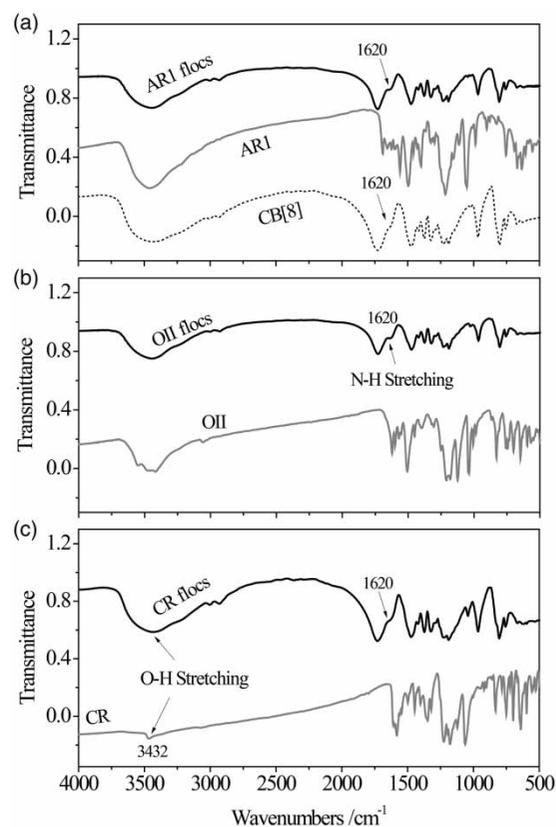


Figure 5 | FT-IR spectrums of AR1, OII, CR, and their corresponding flocs formed in coagulation at pH 6.0.

three studied hydrophilic azo dyes, CR had the largest molecular weight and the most active groups (-NH₂) that could form hydrogen bonds with CB[8] (Table 1), which led to the highest color removal rate and least influence of pH in the coagulation process. Although the coagulation performance of CB[8] varied with the structure of azo dyes, and chemical sludge disposal and economic costs were not considered, this study does provide an alternative method for the coagulation of AR1, OII, and CR wastewaters in a wide pH range.

CONCLUSIONS

Dye wastewater has attracted considerable attention because of its wide range of pH and high content of salts. In this study, the coagulation performance of CB[8] for the removal of color from AR1, OII and CR synthetic wastewaters was investigated. At a given coagulant dosage, the optimum color removal was reached when the zeta potential of the selected dyes was close to 0 mV. Compared with alum, the removal rate of color by CB[8] was less affected

by solution pH. Increases in ionic strength reduced the thickness of the hydrate sphere surrounding the dye molecules and, thus, led to the enhanced removal of color in coagulation. Findings also showed that the removal of AR1, OII and CR primarily depended on the bridging effects of hydrogen bonds and inclusion complexes formed between the dye molecules and CB[8]. Because of the existence of such adsorption bridging actions, positive charges on the molecules of CB[8] could neutralize the negative charges on the dye molecules under acidic conditions. The relatively larger molecular weight and more active substituent groups of CR compared with AR1 and OII enabled its highest removal rate under the same coagulation conditions. Although the coagulation performance of CB[8] varied with the structure of azo dyes, a high color removal efficiency could be achieved without pH adjustment, which enabled CB[8] to be used as an alternative coagulant for the treatment of dye wastewater.

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