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Research of Victoria Blue B Wastewater by Coagulation and Co-Precipitation

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Dying industrial wastewater has become a major problem in the modern industrial water treatment, owing to their complex structures, bio-refractory, anti-oxidation, anti-photolysis and strong heat stability. Thus, treatment of dye wastewater has attracted the attention of researchers all the time. The focus of this work is removal effect of 2,4,6-trimercaptotriazine and aluminum sulfate independent action and synergistic effect on Victoria blue B. The removal effect with different factors, such as the dosage of 2,4,6-trimercaptotriazine or aluminum sulfate, pH value, temperature and other conditions, were investigated and the removal mechanism was discussed. The results show that the decolour treatment of Victoria blue B dye wastewater can achieve the ideal effect by the synergistic effect of 2,4,6-trimercaptotriazine and aluminum sulfate.

Keywords: Victoria blue B, 2,4,6-Trimercaptotriazine, Aluminum sulfate, Removal.

INTRODUCTION

Dye has a considerable impact on both the human being and environment in water because of its more kinds, high organic pollutant content, complicated components, chromaticity and great toxicity. Thus the dye wastewater is the serious environmental problem that needs to solve urgently. Victoria blue B (VBB Fig. 1) is widely used as a dye in the modern industry, which is highly toxic and proven dangerous even at very low concentrations in both aquatic and terrestrial ecosystems. Being a persistent substance, mercury can build up in living organisms, inflicting increasing levels of harm through food chain to higher order species such as human. Therefore, the research on the treatment of Victoria blue B dye wastewater has an important significance.

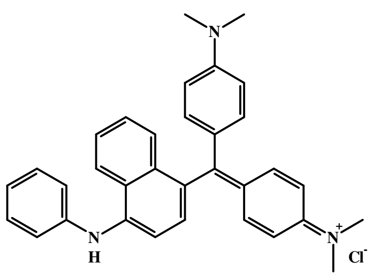

Fig. 1. Molecule structure of Victoria blue B

Victoria blue B belongs to aromatic hydrocarbon, containing cation dyes as a wastewater, their current removal methods are physico-chemical adsorption method and photocatalytic oxidation. The fine performance activated carbon and resin are always used as adsorbent, however, their price and regeneration cost are very high. Recently, scholars devote to research and develop new efficient and low price adsorbent, such as rice husk[1-3], bentonite[4], wheat straw[5,6], soybean hull[7], coconut shell[8,9], orange peel[10], pine[11], seaweed[12], rectories[13], bagasse[14-16], *etc*. But they always need to be modified and activated carbon, or are restricted by producing areas. The ordinary light source of photocatalytic oxidation is ultraviolet and the catalysts are TiO_2, H_2O_2 and so on. In addition, the synergistic degradation of photo-catalytic oxidation and Fenton reagent is used to degrade dye wastewater. These two methods have an obvious effect, but it is limited by catalyst and pH value, it is rare to employ only one method in the whole treatment[17-20]. Ozone oxidization method has a better decolorization result towards dye wastewater, but because of its high treatment cost, therefore, it is very difficult to apply in wastewater treatment[21]. Moreover, white rot fungi has strong ability of decolorization and degradation, however, it is particular about its growing environment and limiting its application in some countries and regions[22].

2,4,6-Trimercaptotriazine (TMT) is an environment-friendly organic sulfur chelating agent for chemically precipitating divalent and univalent heavy metals, such as Ni^{2+}, Pd^{2+}, Cu^{2+}, Ag^{+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ti^{2+} and Pb^{2+} from water[23-29]. Recently, 2,4,6-trimercaptotriazine was widely used to treatment heavy metals in water. Liao *et al.*[30] treated copper ammonia complex by using TMT-15, the results show that 2,4,6-trimercapto-triazine could strongly chelate copper ion, forming precipitate. Hou and Wu[31] used TMT-18F to comprehensively dispose Ag^{+}, Hg^{2+}, Pb^{2+} and Mn^{2+} in the wastewater. The sewage is up to water treatment standards in 0.5 h. Tong[32] and Tang *et al.*[33] testified 2,4,6-trimercaptotriazine as the advanced treatment agents to remove trace Cu^{2+} from water. The results showed that 2,4,6-trimercaptotriazine was the comparatively ideal capture agent of low-level Cu^{2+} *etc*. Deng *et al.*[34] trapped Ag^{+}, Hg^{2+} and Pb^{2+} in wastewater by using TMT-18 and the removal ration is over 99 %; Mo[35] prepared a porous macromolecule filter plate containing 2,4,6-trimercaptotriazine, with the efficiency of removing lead ion above 90 %. The porous macro-molecule filter plate can be reused as well; Xie[36] adopted TMT-18 and polymeric ferric sulfate (PFS) to removal arsenic and lead ions in alkaline industrial wastewater, which realized the combination precipitation and coagulation.

After reviewing the literature, 2,4,6-trimercaptotriazine (TMT), as an environment-friendly water treatment agent, has been widely used to treat heavy metal ions in water, but there is less report on dye treatment using 2,4,6-trimercaptotriazine. There is a reason as follow: almost all reactions are based on complex precipitation. However, 2,4,6-trimercaptotriazine, as an organic sulfur chelating agent, has electronegativity polar (lone pair electrons). It should be discussed and verified that whether 2,4,6-trimercaptotriazine can remove the positive charge organic. Therefore, the current paper took the cationic dyes Victoria blue B as a study object, systematically studied the removal process, discussed the synergistic effect of the flocculant aluminum sulfate, studied the effects of some factors (such as reaction time, pH value, dosage of 2,4,6-trimercapto-triazine and aluminum sulfate (AS) and temperature.) on removal efficiency of Victoria blue B by 2,4,6-trimercapto-triazine and analyzed the mechanism of 2,4,6-trimercapto-triazine and aluminum sulfate treatment Victoria blue B.

EXPERIMENTAL

UV-visible spectrophotometer model UV-2450 was purchased from Shimadzu Co. (Tianjin, China). Digital pH meter model DELTA320 was purchased from Mettler Toledo Company (Shanghai, China). Electronic balance model BS224S was purchased from Sartorius Instrument Systems, Inc. (Beijing, China). Electric blastdrying oven model CS101-AB was purchased from Chongqing test equipment factory, (Chongqing, China). Low speed table centrifuge TDL-60B was purchased from Shanghai Anting science instrument factory, (Shanghai, China). TMT-15 (CP) was purchased from Borendy Co. (Wuhan, China). Victoria blue B (AR) was purchased from Shanghai model plant specimens (Shanghai, China). Aluminum sulfate (AR) was purchased from Xi'an chemical reagent plant (Xi'an, China). The other chemicals are all analytically pure and redistilled water is used in all experiments.

Preparation of Victoria blue B standard solution: Victoria blue B standard solution was prepared by dissolving 1 g Victoria blue B in 1000 mL redistilled water to make into 1 g/L reserving liquid. The solution was stored 1-2 days to completely dissolve, making sure the absorbance of the solution stable. The targeting concentration was prepared after diluted and placed 1 h.

Preparation of 2,4,6-trimercaptotriazine (TMT) standard solution: 2,4,6-Trimercaptotriazine (TMT) standard solution was prepared by dissolving 10 mL TMT-15 standard solution to 1000 mL volumetric flask to obtain a constant concentration of 2,4,6-trimercaptotriazine 11.2 g/L.

Experimental method: Take quantitatively Victoria blue B solution and 2,4,6-trimercaptotriazine aluminum sulfate (AS) into the conical flask and wave fully. Change experimental conditions, such as pH value and temperature. The centrifuge condition is rotation speed 4000 r/min and time 10 min. The supernatant is used to detect the concentration of residual Victoria blue B dye by the spectrophotometer method in a certain time, which is used to calculate the degradation rate of Victoria blue B.

Standard curve of Victoria blue B: Take different concentrations Victoria blue B solution as the samples against secondary distilled water, change wavelength and scanning spectrum. The maximum absorption was obtained at 616 nm. Measure the absorbance of Victoria blue B solution at 616 nm to calculate the degradation rate of Victoria blue B. The calculation formula is as follow:

$$\eta = (C_0-C)/C_0 \times 100\ \% \quad (1)$$

$$A = \varepsilon bc \text{ (Beer's law)} \quad (2)$$

$$\eta = (A_0-A)/A_0 \times 100\ \% \quad (3)$$

where C_0 (mg/L) and C (mg/L) are the initial and residual concentration of Victoria blue B, respectively.

When the degradation rate of Victoria blue B is more than 99 %, Victoria blue B is considered to be completely removed.

RESULTS AND DISCUSSION

Choice of 2,4,6-trimercaptotriazine optimum dosage: The concentration of Victoria blue B dye solution was 80 mg/L in this experiment. Fig. 2 illustrated that the reaction reached stable in 6 h. Adding 896 mg/L 2,4,6-trimercaptotriazine into Victoria blue B dye solution, the maximum degradation rate achieved with 97.47 %. The removal rate increased with the increase of dosing quantity of 2,4,6-trimercaptotriazine in the reaction system. The maximum degradation rate achieved with the 2,4,6-trimercaptotriazine dosage of 896 mg/L. When the dosage was more than 896 mg/L the degradation rate of Victoria blue B was decreased with the increase of 2,4,6-trimercapto-triazine.

When the dosing quantity of 2,4,6-trimercaptotriazine was less, the concentration of 2,4,6-trimercaptotriazine was small and the binding capacity of 2,4,6-trimercaptotriazine and Victoria blue B was weak. Therefore, the degradation activity for Victoria blue B was poor. With the increase of dosing quantity of 2,4,6-trimercaptotriazine, the concentration of 2,4,6-trimercaptotriazine particle was continuously increasing. Thus their binding capacity with degraded material Victoria blue B was stronger and the removal activity was enhanced. How ever, because of the obscuring effect between particles, when the dosing of 2,4,6-trimercaptotriazine increased to a

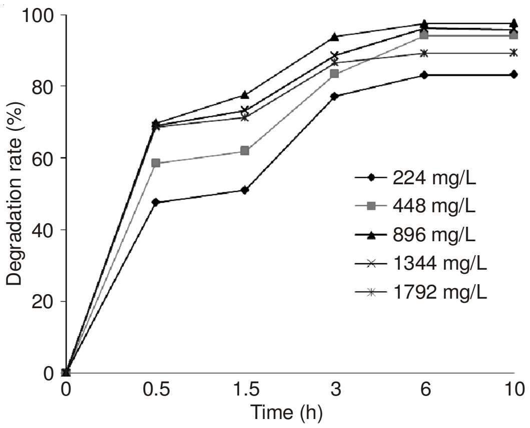

Fig. 2. The choice of 2,4,6-trimercaptotriazine optimum dosage

certain quantity, the obscuring effect among 2,4,6-trimercaptotriazine particles was increasingly serious, causing that 2,4,6-trimercaptotriazine particles couldn't fully play their degradation effect owing to their inadequacy contact, finally, resulting in the waste of 2,4,6-trimercaptotriazine, therefore, the degradation rate of Victoria blue B was decreased.

Dhoice of aluminum sulfate optimum dosage: Fig. 3 showed that when the concentration of Victoria blue B dye was 80 mg/L, the reaction reached stable in 6 h. Adding 100 mg/L aluminum sulfate into Victoria blue B dye solution, the maximum degradation rate achieved 49.36 %. After adding coagulant aluminum sulfate into the water, a large amount of hydroxide precipitation and flocculating constituents produced in coagulation process. These flcos and Victoria blue B increased the concentration of the water particle, which advanced enormously the aggregation among Victoria blue B, thus, Victoria blue B particles were clustered together massivly that resulted to the effect of solid-liquid separation. A large number of Victoria blue B particles fell into the flocs and sediment that were increase constantly and they were precipitated. It played the best role for aluminum sulfate in coagulation-flocculation effect to remove a part of Victoria blue B dye from wastewater.

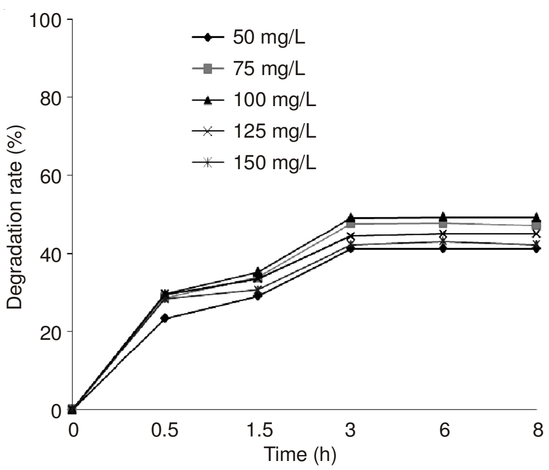

Fig. 3. The choice of aluminum sulfate optimum dosage

Choice of aluminum sulfate optimum dosage under the synergistic effect: Fig. 4 showed that the optimal concentration of aluminum sulfate was 25 mg/L, when Victoria blue B dye and 2,4,6-trimercaptotriazine were 80 and 896 mg/L, respectively and the reaction reached stable in 3 h and the maximum degradation rate was up to 99.21 %.

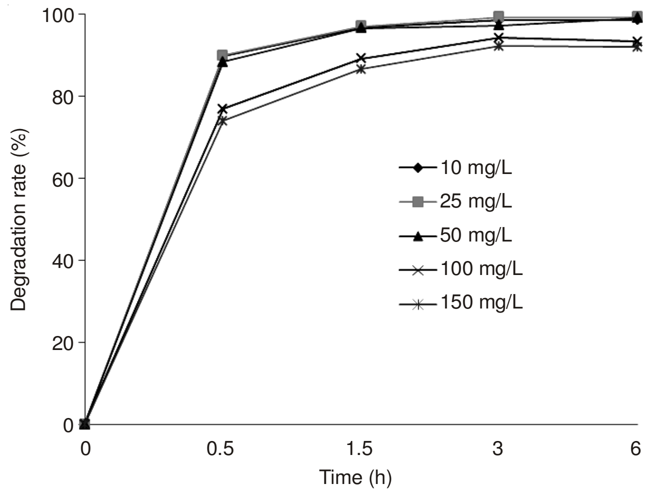

Fig. 4. The choice of aluminum sulfate optimum dosage under the synergistic effect

From Fig. 2, the optimal dosing quantity of 2,4,6-trimercaptotriazine was 896 mg/L. When Victoria blue B dye was degraded only by 2,4,6-trimercaptotriazine (TMT), the reaction reached stable in 6 h and the degradation rate was 97.47 %. From Fig. 3, the dosing quantity of aluminum sulfate was 100 mg/L. When Victoria blue B dye whose concentration was 80 mg/L was degraded only by aluminum sulfate, the reaction reached stable in 6 h and the degradation rate was only 49.36 %. That's because aluminum sulfate have a certain absorptive effect to Victoria blue B dye in the solution, which leaded to the decrease of the content of Victoria blue B dye to a certain extent. Consequently, we consider that the degradation effect of aluminum sulfate alone was poor. While the effect only 2,4,6-trimercaptotriazine was better. However, the synergistic effect of them was the best and the degradation rate was 99.21 %.

When we added coagulant aluminum sulfate into the wastewater with the pincer complex of 2,4,6-trimercaptotriazine and Victoria blue B, the flocculant effect produced as follow[37]: (1) The combined-state coagulant agent could be strongly adsorbed on the surface of sediment particles in the solution and then, condensation can be produced by surface complexation and ion exchange adsorption with sediment particles. (2) Hydroxide precipitation flcos was the hydrolysate of coagulant, which has the sweep flocculation effect on particulate matter.

Determination of the optimum pH in the removal action: As inferred from Fig. 5, when the concentration of Victoria blue B dye was 80 mg/L, 2,4,6-trimercaptotriazine's was 896 mg/L, aluminum sulfate's was 25 mg/L, pH value was 10, the reaction reached stable in 1.5 h and the maximum degradation rate achieved at 99.54 %. The degradation rate was greatly increased. Therefore, the optimum pH range was 8-12 in the ternary mixtures of Victoria blue B, 2,4,6-trimercaptotriazine and aluminum sulfate.

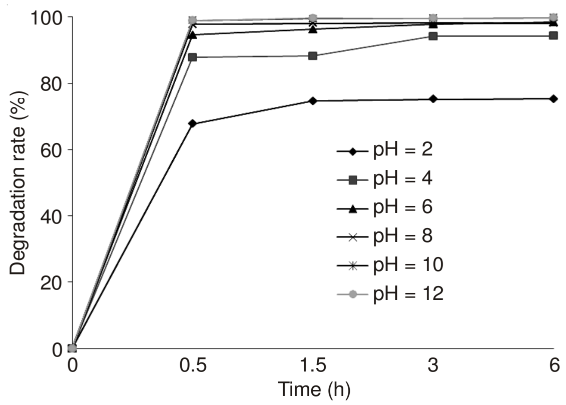

Fig. 5. Determination of the optimum pH

Determination of the optimum temperature in the removal action: It was manifested from Fig. 6 that the reaction could reach stable in 0.5 h, when the concentration of Victoria blue B dye was 80 mg/L, 2,4,6-trimercaptotriazine's was 896 mg/L, aluminum sulfate's was 25 mg/L, pH value was 10. When the temperature was 20-60 °C, the degradation rates of Victoria blue B dye were all more than 99%. The degradation rate 99.23 % at 20 °C, it is considered that Victoria blue B was completely removed. Therefore, the optimum temperature was room temperature in the ternary mixtures of Victoria blue B, 2,4,6-trimercaptotriazine and aluminum sulfate and the concentration of Victoria blue B dye was 80 mg/L.

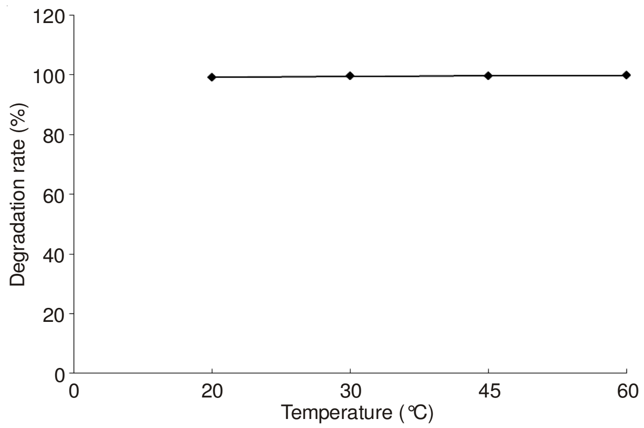

Fig. 6. Determination of the optimum temperature

Analysis for mechanism: 2,4,6-Trimercaptotriazine is successfully used to remove Victoria blue B in the dye wastewater and the mechanism is analyzed as follows: there are strong positive charges on the surface of Victoria blue B dye molecular structure in wastewater dispersion system and the forms of the strong positive charges result in soluble molecules of Victoria blue B dye are difficult to degrade in the nature and keep long-term stable in water. 2,4,6-trimercaptotriazine, as an organic sulfur chelating agent, has negative polarity. Its charges are opposite to Victoria blue B dye particle and the opposite charges attract each other, leading to some major granular structures and precipitation owing to neutralize. Aluminum sulfate is an inorganic coagulant and has good coagulant capacity. aluminum sulfate can further adsorb the small fragmented pieces of precipitation which has formed in solution, join together and bond to form the larger particles and floccules. It plays a positive role in degrading Victoria blue B by 2,4,6-trimercaptotriazine. Therefore, the removal of Victoria blue B by 2,4,6-trimercaptotriazine is based on the opposite charges of two substances which attract each other to form precipitate. The synergistic effect of aluminum sulfate coagulant remarkably increased the degradation efficiency of 2,4,6-trimercaptotriazine and Victoria blue B is removed in maximum extent, under the synergistic effect of both together.

Conclusion

2,4,6-Trimercaptotriazine is successfully used to remove Victoria blue B in the dye wastewater. The optimum conditions for the removal are as follow: when the concentration of Victoria blue B dye was 80 mg/L, Victoria blue B dye the dosage of 2,4,6-trimercaptotriazine is 896 mg/L, the dosage of aluminum sulfate is 25 mg/L, pH range was 8-12 and the temperature is room temperature. The removal mechanism is described as follows: the charges of the two substances are opposite and they attract each other, then precipitating and coagulation aluminum sulfate (AS). Victoria blue B is removed at the most extent with the synergistic effect of both together.

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