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Electronic Supplementary Information (ESI)

A rapid potentiometric titration method for measuring low-level chemical oxygen demand in organic wastewater containing the synthetic phenothiazine dyes

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1. Preparation of the solution

The 2.00 mM $(NH_4)_2Fe(SO_4)_2$ (FAS) was used as titrant, and the 5.00 mM $KMnO_4$ and $Ce(SO_4)_2$ were simultaneously used as the main oxidants. Note that the $KMnO_4$ and $(NH_4)_2Fe(SO_4)_2$ solution must be calibrated against the reference reagents according to requirements of the national standard method [1, 2]. The 0.01 M solution of potassium persulfate used as an assisted oxidation reagent was prepared by dissolving a certain amount of $K_2S_2O_8$ into 0.01 M NaOH solution.

In addition, the three kinds of substances as the digestion catalysts would be introduced to the digestion process, whose chemical formulas are $CuSO_4$, Ag_2SO_4 and $MnSO_4$, respectively. Specifically, the adequate amount of solid powder of $CuSO_4$•$5H_2O$ and Ag_2SO_4 is dissolved in 0.9 M H_2SO_4 solution to make the working solution of 0.01 M $CuSO_4$ and 0.0075 M Ag_2SO_4, respectively. The working solution of 0.01 M $MnSO_4$ was made by dissolving the appropriate amount of $MnSO_4$•H_2O into 0.05 M H_2SO_4 solution. Lastly, because potassium tungstate that could inhibit the thermal decomposition reaction of potassium permanganate will be necessary; a certain amount of K_2WO_4 was dissolved in water to make its working solution of 0.005 M for use.

The stock solution of methylene blue (MB) was prepared by dissolving 11.7 mg MB material ($C_{16}H_{18}N_3SCl{\cdot}3H_2O$) with water in a 100 mL volumetric flask, and must be treated with ultrasonic wave for 40 minutes in order to ensure its MB mass concentration up to 100 mg L^{-1}. Then, the standard MB sample solutions with the different COD values could be gotten by the appropriate dilution of MB stock solution prior to use.

According to the oxidation reaction equation of MB, we could be calculated that the actual MB solution per a mass concentration unit of 1.00 mg L^{-1} had an equivalent COD_{Theor} value of 1.924 mg O_2 L^{-1}. Similarly, we could prepare these working solution of glucose (purity 99.5%) and TB (purity 89.5%), in which each mass concentration unit of 1.00 mg L^{-1} should gain their equivalent COD_{Theor} value of 1.062 and 1.685 mg O_2 L^{-1}, respectively. [4]

2. The optimization of added amounts of catalytic reagents in two digestion solutions

To obtain the optimal amount about the catalytic reagents added in the alkaline digestion solution and acidic digestion solution, we selected a standard MB sample as probe to verify the degradation capability in each digestion reaction. In the alkaline digestion step, the optimum amounts of added chemical reagents for completely decomposing the organic substance per 10.00 mL water sample were as follows:

2.85 mL NaOH (0.05M), 3.75 μmol $MnSO_4$ and 2.20 μmol $K_2S_2O_8$. As shown in **Fig. S1**, the optimized curves about two reagents of NaOH and $K_2S_2O_8$ were provided herein. Moreover, considering the total dosage of 22.5 μmol $KMnO_4$, the applicable dosage of $MnSO_4$ would be ascertained by a molar ratio of 6:1 between $KMnO_4$ and $MnSO_4$.

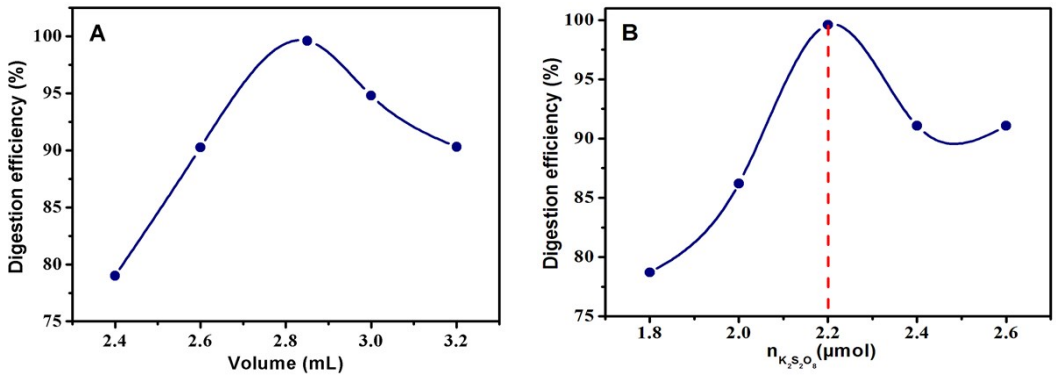

Fig. S1 The dependence of digestion efficiency for a standard MB samples on the amount of added chemical reagents in the alkaline digestion solution. There were two optimization curves for adding volumes of 50 mM NaOH (A), and adding amounts of $K_2S_2O_8$ (B), respectively.

Similarly, we also could ascertain the reagent dosages in the acidic digestion solution, which consisted of 2.20 mL H_2SO_4 (9.0 M), 5.0 μmol K_2WO_4, 7.9 μmol $CuSO_4$ and 2.6 μmol Ag_2SO_4. As shown in Figure S2A and Figure S2B, three optimized curves relating to adding volumes of both H_2SO_4 and K_2WO_4 were provided. In this case, if the molar ratio of 4:3 for the applicable dosage of $Ce(SO_4)_2$ to the sum amounts of $CuSO_4$ and Ag_2SO_4 was fixed as a precondition, the evolutional curve (Figure S2 C) could ascertain the optimal molar ratio of 3:2 between $CuSO_4$ and Ag_2SO_4. Whereas, taking into account the known dosages of 17.5 μmol $Ce(SO_4)_2$, we could actually ascertain the added amounts of both $CuSO_4$ and Ag_2SO_4 (ref. Figure S2C). Obviously, when these optimized experimental conditions for both alkaline digestion solution and acidic digestion solution is brought into effect, we would assure to achieve the complete degradation of MB through the two-step wet-chemical digestion process.

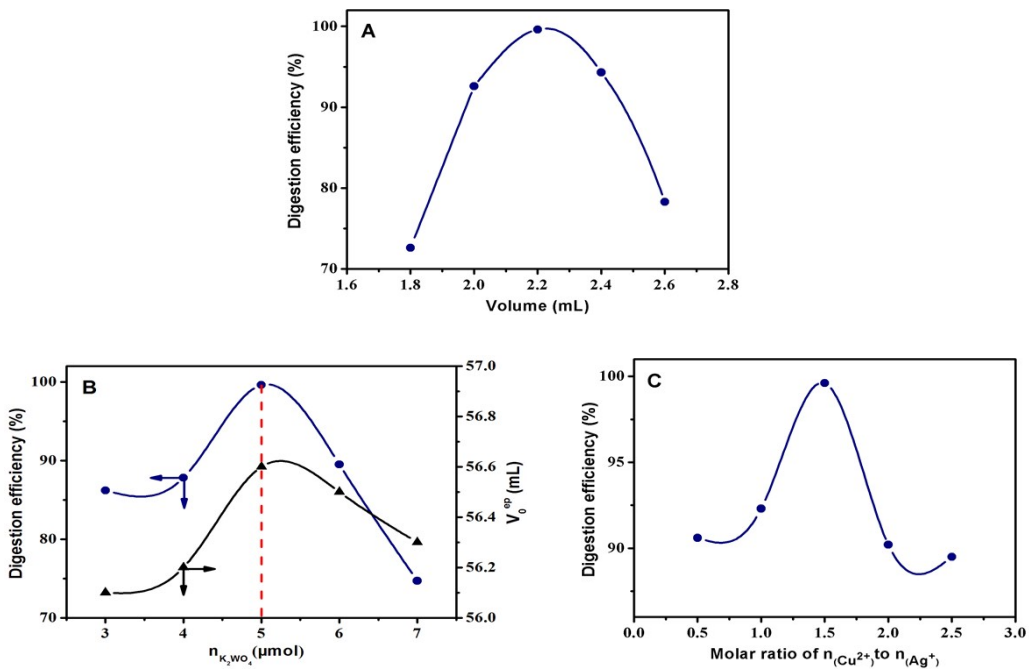

Fig. S2 The dependence of degradation efficiency for a standard MB sample on the added amount of some chemical reagents in the acidic digestion solution. There were three optimization curves for adding volumes of 9.0 M H_2SO_4 (A), adding amounts of K_2WO_4 (B), and the optimal molar ratio of $CuSO_4$ and Ag_2SO_4 (C), respectively.

3. Interference of chloride ions

In order to evaluate the effect of chloride ions on COD values by using this method, we selected the 2.00 mg L^{-1} standard MB sample as probe samples to make the testing experiment, in which the coexistence of chloride ions was set with the various concentrations in the range of 0-800 mg L^{-1}.

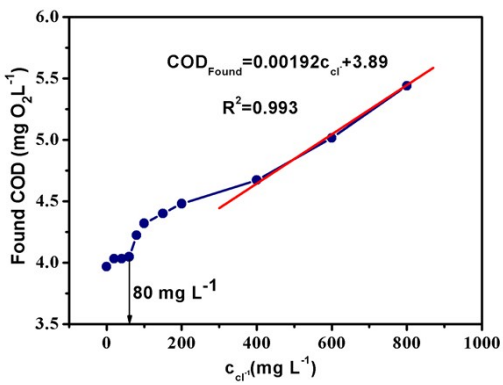

Fig. S3 Effect of coexisting chloride ions on the COD value of a 2.0 mg L^{-1} standard MB sample.

4. The comparing measurement for some standard reference samples

Table S1 Comparison results on the digestion efficiencies between this method and standard potassium dichromate titration method

Standard reference sample	This method			Standard method*		
	COD (mg O_2 L^{-1})		The total digestion efficiency (%)	COD_{Cr} (mg O_2 L^{-1})		The total digestion efficiency (%)
	COD_{Theor} value	COD_{Found} value (mean±S.D., n=3)		COD_{Theor} value	COD_{Found} value (mean±S.D., n=3)	
MB	25.0	24.9 ± 0.21	99.6	25.0	19.1 ± 0.07	76.4
Glucose	25.0	24.9 ± 0.07	99.6	25.0	24.8 ± 0.16	99.2
Glucose + MB	15.0+10.0	24.9 ± 0.10	99.6	15.0+10.0	21.8 ± 0.41	87.2

* Please refer to the document listed as references 2.

References

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