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$_4$)$_2$Fe(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$_4$)$_2$Fe(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$_2$S$_2$O$_8$ 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$_2$SO$_4$ and MnSO$_4$, respectively. Specifically, the adequate amount of solid powder of CuSO$_4$•5H$_2$O and Ag$_2$SO$_4$ is dissolved in 0.9 M H$_2$SO$_4$ solution to make the working solution of 0.01 M CuSO$_4$ and 0.0075 M Ag$_2$SO$_4$, respectively. The working solution of 0.01 M MnSO$_4$ was made by dissolving the appropriate amount of MnSO$_4$•H$_2$O into 0.05 M H$_2$SO$_4$ solution. Lastly, because potassium tungstate that could inhibit the thermal decomposition reaction of potassium permanganate will be necessary; a certain amount of K$_2$WO$_4$ 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$_3$SCl·3H$_2$O) 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$_2$S$_2$O$_8$. As shown in **Fig. S1**, the optimized curves about two reagents of NaOH and K$_2$S$_2$O$_8$ 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](image)

**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$_2$S$_2$O$_8$ (B), respectively.

Similarly, we also could ascertain the reagent dosages in the acidic digestion solution, which consisted of 2.20 mL H$_2$SO$_4$ (9.0 M), 5.0 μmol K$_2$WO$_4$, 7.9 μmol CuSO$_4$ and 2.6 μmol Ag$_2$SO$_4$. As shown in Figure S2A and Figure S2B, three optimized curves relating to adding volumes of both H$_2$SO$_4$ and K$_2$WO$_4$ 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$_2$SO$_4$ 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$_2$SO$_4$. 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$_2$SO$_4$ (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.
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 H₂SO₄ (A), adding amounts of K₂WO₄ (B), and the optimal molar ratio of CuSO₄ and Ag₂SO₄ (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. 

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

<table>
<thead>
<tr>
<th>Standard reference sample</th>
<th>This method</th>
<th>Standard method*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>COD (mg O₂ L⁻¹)</td>
<td>COD₉₀₅ (mg O₂ L⁻¹)</td>
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<td></td>
<td>COD₉₀₅ value</td>
<td>COD₉₀₅ total value</td>
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<tr>
<td>MB</td>
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<tr>
<td>Glucose</td>
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<td>24.9 ± 0.07</td>
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<tr>
<td>Glucose + MB</td>
<td>15.0+10.0</td>
<td>24.9 ± 0.10</td>
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</tbody>
</table>

* Please refer to the document listed as references 2.

References


