Electronic Supplementary Information (ESI)

Accurate Determination of Low-level Chemical Oxygen Demand Using a Multistep Chemical Oxidation

Digestion Process for treating Drinking Water Samples

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1. Preparation of the solution

The 3.00 mM $(NH_4)_2Fe(SO_4)_2$ (FAS) was used as titrant, and the 5.00 mM $KMnO_4$ and $K_2Cr_2O_7$ were simultaneously used as the main oxidants. Note that the $KMnO_4$ and FAS solution must be standardized against the fiducial reagents of sodium oxalate and potassium dichromate,[1, 2] respectively. 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. Sodium chloride was used for chloride interference studies.

In addition, the three kinds of substances as the digestion catalysts would be introduced to the digestion process, whose chemical formulas are $MnSO_4$, $CuSO_4$ and Ag_2SO_4.[3] Specifically, the reasonable amount of solid powder of $CuSO_4 \cdot 5H_2O$ and Ag_2SO_4 was 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 $MnSO_4 \cdot H_2O$ into 0.05 M H_2SO_4 solution.

In this experiment, a stock solution of potassium hydrogen phthalate (KHP) with a theoretical COD value of 500 mg O_2 L^{-1} was prepared by dissolving 0.4250 g of KHP in 1.0 L water, and the testing solutions with the different COD values were prepared by appropriate dilution of the stock solution.

According to the oxidation reaction equation of KHP,[4] it could be calculated that a standard KHP sample with the mass concentration of 1.0 mg L^{-1} was the equivalent of 1.175 mg O_2 L^{-1} of its theoretical COD value. Similarly, it also was obtained that the standard sample containing 1.0 mg L^{-1} of glucose and glycine were the equivalent of 1.066 and 0.639 mg O_2 L^{-1} of their theoretical COD value, respectively. So, the mixed standard substance sample with the total theoretical COD value of 300 mg O_2 L^{-1} could be prepared by dissolving 0.0851 g of KHP, 0.0938 g of glucose and 0.1565g of glycine in 1.0 L purity water, and appropriately diluted prior to use.

2. The optimization of added amounts of catalytic agent in the digestion solutions

To optimize the most appropriate amount about catalytic agent added in the alkaline digestion solution and acidic digestion solution, we selected the KHP standard sample as probe to verify the degradation efficiency of a digestion reaction. As shown in Fig. S1, in the alkaline digestion procedure, the optimum amounts of added chemical agent for completely decomposing the organic substance per 10.00 mL water sample were as follows: 3.30 mL NaOH (50 mM), 2.50 μmol $K_2S_2O_8$ and 9.00 μmol $MnSO_4$. Moreover, considering the added amount of 22.5 μmol $KMnO_4$, we could obtain a present 2.5:1 stoichiometric relationship with the molar ratio of $KMnO_4$ to $MnSO_4$.
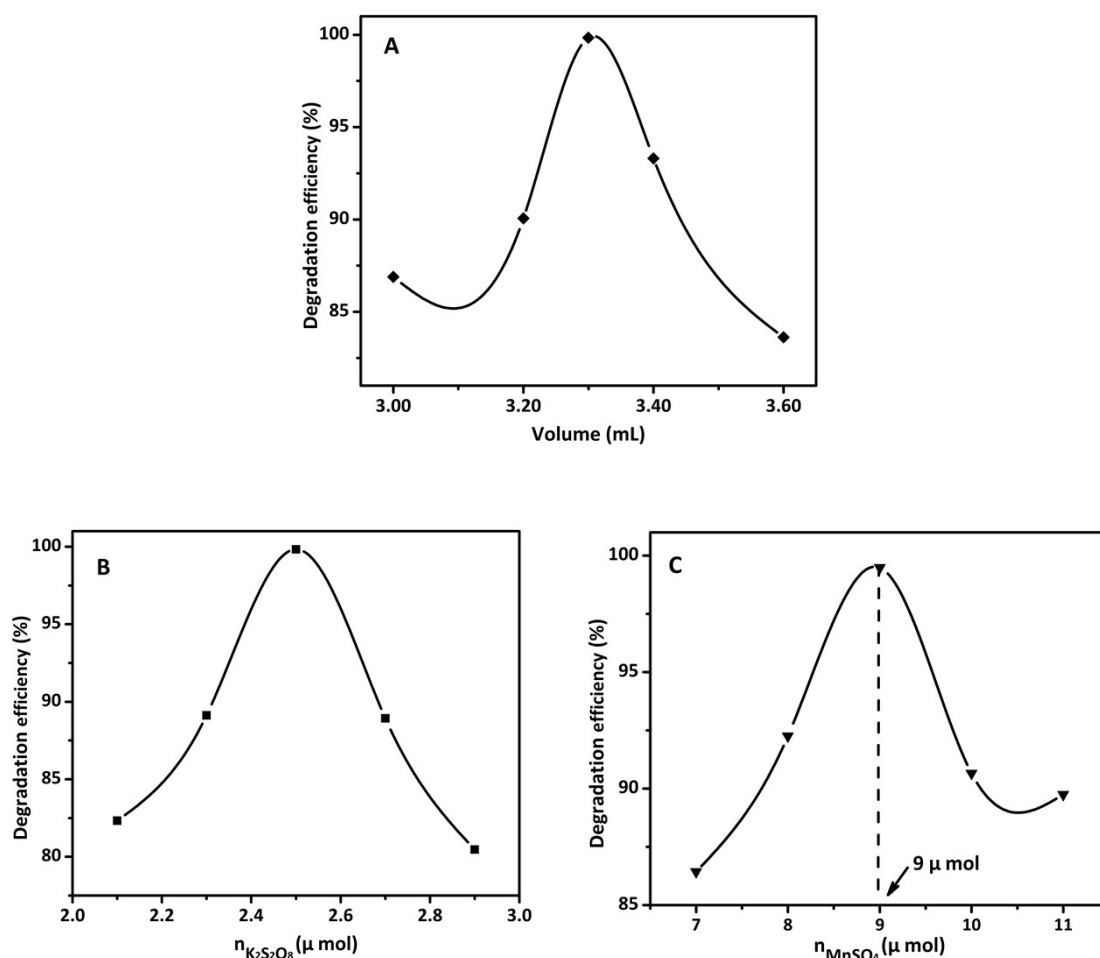
Fig. S1 The dependence of degradation ratio for KHP standard samples on the amount of added chemical agent in the alkaline digestion solution. There were the optimal volumes of 50 mM NaOH (A), the optimal amounts with a mole number unit of $K_2S_2O_8$ (B) and $MnSO_4$ (C), respectively.

Similarly, as shown in Fig. S2, we optimize the chemical agent amount added in the acidic digestion solution. The results indicated that as soon as 2.40 mL H_2SO_4 (9.0 M), 9.0 μmol Cu^{2+} and 13.5 μmol Ag^+ were added into the digested sample through the first-step alkaline digestion procedure, the total degradation ratio of the KHP compound ultimately reached to 100% over the whole digestion process. Thus, considering the added amount of 11.25 μmol $K_2Cr_2O_7$, we also could obtain a present 1:2 quantitative relationship with the molar ratio of $K_2Cr_2O_7$ to the sum of Cu^{2+} and Ag^+. Note that there were the 3:2 molar ratio relationships between the amounts of two catalytic agents Ag^+ to Cu^{2+}.
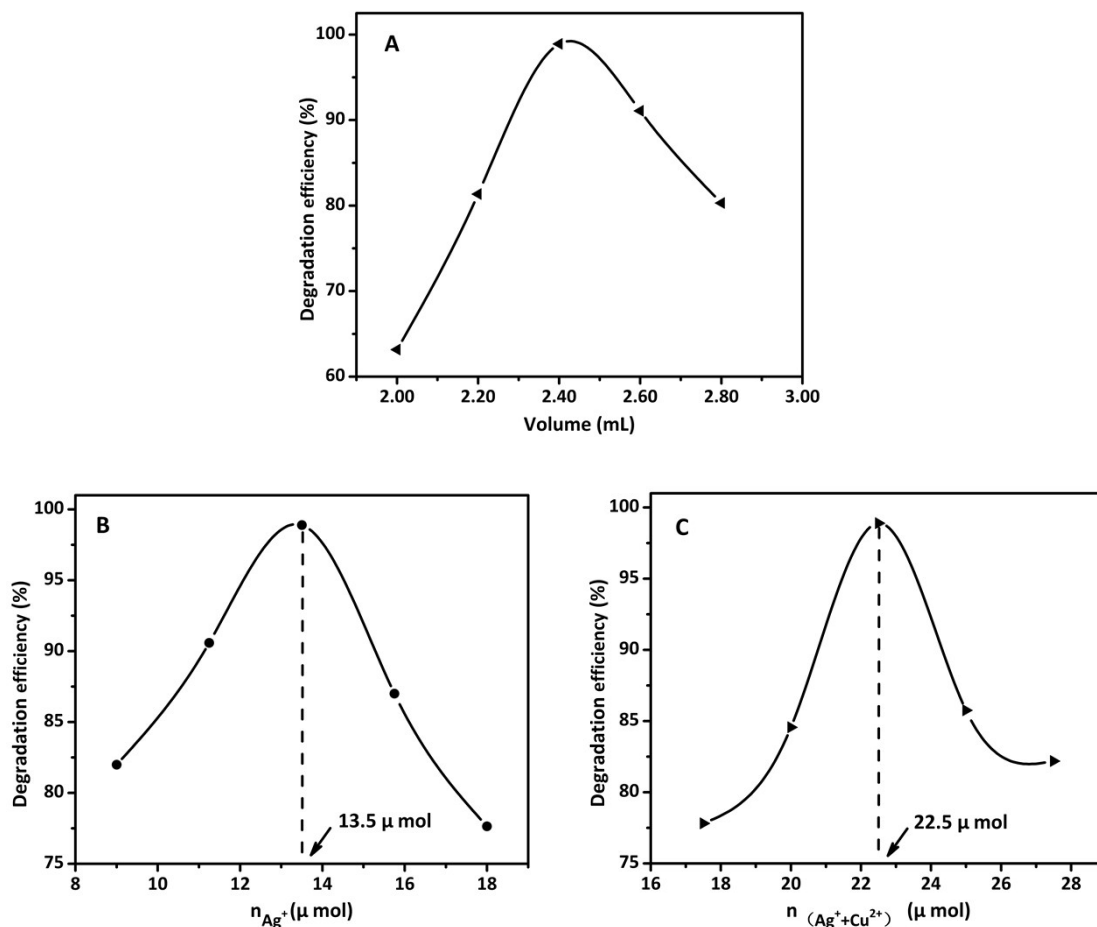
Fig. S2 The dependence of degradation ratio for KHP standard samples on the amount of added chemical agent in the acidic digestion solution. There were the optimal volumes of 9.0 M H_2SO_4 (A), the optimal amounts of Ag^+ with the constant addition of 9.0 μmol Cu^{2+} (B) and the optimal sum amounts of Cu^{2+} and Ag^+ (C).

3. Comparison of the proposed method and the standard method

Table S1 gives the comparison COD results in the real water samples of tap water and bottled water for the proposed method and the standard acidic permanganate index method.[1] According to the water quality-determination method of permanganate index for the examination of drinking water and surface water (GB11892-89, Open Reflux, Titration Method) from SEPAC (P.R. China), we have measured the COD_{Mn} indexes in the real water samples under the regulation condition with the different addition amount of some standard substances. But, since the standard method has just offered a practical COD_{Mn} limits of quantification (LOQ) in 0.5-4.5 mg O_2 L^{-1} as the sampling volume of water sample is restricted on 100.0 mL, the COD results, as seen in Table S1, will righteously verify the distinction between the proposed method and the open reflux standard titration method for the routine analysis of drinking water samples. Specifically, this novel method not

only exhibits a less relative standard deviation (RSD) for ultra-low COD water sample, but also possesses the high recovery in a wider linear range of COD values.

Table S1 Comparison of the proposed method and the open reflux standard method for real water samples

Water sample	This method					Standard method				
	COD (mg O_2 L^{-1})				The average recovery (%)	COD_{Mn} (mg O_2 L^{-1})				The average recovery (%)
	Original COD (n=3, P=0.95)	RSD (%)	Added COD	Found COD (n=3, P=0.95)		Original COD (n=3, P=0.95)	RSD (%)	Added COD	Found COD (n=3, P=0.95)	
Tap water 1	3.07±0.10	1.4	2.00[a]	5.02±0.11	97.5	2.25±0.10	1.7	2.00[a]	4.52±0.10	113.5
			2.00[b]	4.95±0.29	94.0			2.00[b]	4.34±0.05	104.5
			10.00[a]	12.8±0.20	97.1			10.00[a]	4.72±0.10	**24.7**
Tap water 2	3.00±0.12	1.7	2.00[a]	4.98±0.10	99.0	1.99±0.18	3.6	2.00[a]	4.07±0.11	104.0
			2.00[c]	4.99±0.13	99.5			2.00[c]	3.97±0.13	99.0
Bottled water	0.42±0.04	3.5	1.50[b]	1.84±0.10	94.7	0.43±0.10	**8.8**	1.50[b]	2.02±0.08	106.0
			1.50[c]	1.90±0.06	98.7			1.50[c]	1.90±0.15	98.0

* The superscript (a, b and c) represents the additional substances of KHP, phenol and glucose, and their theoretical COD value were the equivalent of 1.175, 2.380 and 1.066 mg O_2 L^{-1} per mass content units of 1.00 mg L^{-1} , respectively.

References

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2. *Water quality-determination of the chemical oxygen demand-dichromate method.* The State Environmental Protection Administration of China, National Standard GB 11914-89, China, 1990.

3. K. B. Suresh, T. James, P. Jaidev, F. Karl, B. A. Deepak and C. G. Stephen, *Ind. Eng. Chem. Res*., 2006, **45**(4), 1221-1258.

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