Views & Comments

Catch Me If You Can: Chemical Adulteration in Wastewater Compliance Testing

Liping Liu[1,2], Puqi Jia[1,*], Jie Han[2,*]

1. Department of Environmental Science and Engineering, College of Earth and Environmental Sciences, Lanzhou University, Lanzhou 730000, P.R. China

2. Department of Environmental Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, P.R. China

*Corresponding authors. Emails: jpq@lzu.edu.cn (P. Jia); jiehan@xjtu.edu.cn (J. Han), ORCID: https://orcid.org/0000-0001-6790-0650

Abstract

A new legislative framework issued by the Ministry of Ecology and Environment of China prohibits any intentional use of 'interfering agent' during wastewater compliance testing. For the first time, such practices are brought to public attention, although they have been barely discussed in scientific literature. Targeting the dichromate method in chemical oxygen demand (COD) testing, a standard method widely adopted by regulatory agencies, the sodium chlorate-based 'COD remover' lowers measurements by oxidizing organic pollutants in samples under acidic and high-temperature conditions. Based on its reactions, the interfering agent only works under the testing conditions, and does not function as an effective treatment in wastewater under normal conditions. The use of 'COD remover' may have created an underground industry, where users can anonymously purchase those products in 25-Kg packages from all major domestic online retailers in China. A notable case was recently publicized under the new legislation, where 131 tons of 'COD remover' had been used in a municipal wastewater treatment plant. However, little is known about the prevalence of its use, in China or other geographic regions, and whether COD is the only targeted indicator in wastewater compliance testing. Nitrites function as interfering agents in the iodometric method for measuring dissolved oxygen in wastewater. There are also reports of chemical adulteration in online monitoring of gas emissions. The specific reactions and mechanisms involved in compliance testing methods provide inherent vulnerability for targeted chemical adulteration. There is a need to develop more robust and adulteration-proof methods for wastewater and other environmental compliance testing.

Keywords: Chemical oxygen demand, effluent discharge, sodium chlorate, interfering agent; dissolved oxygen; iodometric method

On December 14, 2020, the Ministry of Ecology and Environment of China (MEEC) introduced a new legislative framework for treatment and management of urban wastewater. For the first time, practices such as intentional use of chemical reagents as interfering agents for manipulation of testing or monitoring data during wastewater compliance testing are deemed illegal (MEEC, 2020a). One month later, MEEC published findings from an investigation at a municipal wastewater treatment plant where the operators routinely used 'COD remover' as a chemical adulterant to interfere with the compliance testing of wastewater effluent quality, the first legal action taken against such practices in the nation under the new legislation (MEEC, 2021). The underground industry of compliance-targeted wastewater chemical adulteration has surfaced to public attention.

Chemical oxygen demand (COD) is one of the most widely used indicators on the loading of oxidizable organic pollutants in wastewater (BS, 1988; DIN, 1986; EPA, 1993; ISO, 1989, 2002; MEEC, 2017a, b; UNE, 2002). For instance, for most types of industrial wastewater in China, the maximum limit of COD level is 50–150 mg/L for treated effluent discharge (MEEC, 2011, 2012, 2020b). Specifically, the dichromate method is most commonly adopted for measuring COD levels in wastewater due to its ability to degrade a wide range of organic pollutants (Zhao et al., 2004). It is also the current standard testing method specified by various authorities and organizations including the US EPA (Method 410.4, Rev 2.0) (EPA, 1993), the MEEC (HJ 828–2017 and HJ 924-2017) (MEEC, 2017a, 2017b), the International Organization for Standardization (ISO 6060:1989 and ISO 15705:2002) (ISO, 1989, 2002), the British Standards Institution (BS 6068-2.34:1988) (BS, 1988), the German Institute for Standardization (DIN 38414-9:1986) (DIN, 1986) and the Una Norma Espanola (UNE 77004:2002) (UNE, 2002) for measuring COD levels in wastewater. The use of chemical adulterants, however, is to interfere with the testing results during regulatory inspections when the COD level of the discharged effluent does not meet the current quality standards.

Currently known practices of chemical adulteration in wastewater compliance testing mainly involve the use of a chemical product ambiguously labeled as 'COD remover'. The product, which contains sodium chlorate ($NaClO_3$) as its main ingredient, lowers the COD values measured by the dichromate method during wastewater compliance testing (MEEC, 2020b). By oxidizing organic pollutants in wastewater under standard testing conditions (*e.g.*, 30 min acid digestion at 165 °C) (MEEC, 2017a), sodium chlorate acts as an interfering agent in COD measurements under the current testing protocols. The following reactions take place in the presence of sodium chlorate under the testing conditions, where *R* denotes organic pollutants present in wastewater samples and *RO* denotes degradation intermediates after oxidation.

$$4Cl^{-} + Hg^{2+} \rightarrow HgCl_4^{\ 2-} \tag{1}$$

$$Cr_2O_7^{\ 2-} + R \rightarrow Cr^{3+} + RO\,/\,CO_2 \tag{2}$$

$$Cr_2O_7^{\ 2-} + RO \rightarrow Cr^{3+} + CO_2 \tag{3}$$

$$ClO^{3-} + R + H_2SO_4 \rightarrow ClO_2 + H(SO_4)^{-} + RO\,/\,CO_2 \tag{4}$$

$$ClO_2 + R \rightarrow RO + Cl^{-} \tag{5}$$

$$4Cl^{-} + Hg^{2+} \rightarrow HgCl_4^{\ 2-} \tag{6}$$

The presence of sodium chlorate can have dramatic influences on the COD testing results in samples analyzed by the dichromate method. In the heated concentrated acid solutions during the digestion process, chlorate anions (ClO_3^{-}) quickly undergo a reduction and transform into chlorine dioxide (ClO_2), an oxidizing gas generated from reactions between $NaClO_3$ and organic pollutants in the wastewater sample (Deshwal and Lee, 2004). Most organic substances, including persistent compounds, can be quickly oxidized by ClO_2 (Huber et al., 2005). The redox reactions initiated by $NaClO_3$ and ClO_2 reduce the total consumption of dichromate anions ($Cr_2O_7^{2-}$) by organic matter present in the wastewater sample, and subsequently lowers the COD measurements under the test conditions. Experimental results on simulated wastewater samples using benzohydroxamic acid showed that the addition of $NaClO_3$ consistently reduced COD measurements from 214 mg/L to below 100 mg/L using the dichromate method, when the concentration of $NaClO_3$ reached 600 mg/L in the samples tested (Meng et al., 2019). However, COD reductions were only observed under the testing conditions, while the COD levels kept intact under the normal conditions (Meng et al., 2019).

In China, commercial products labelled as 'COD remover' with the appearances of white to pale yellow crystalline solids similar to that of sodium chlorate are often sold in bulk quantities (*e.g.*, 25 Kg bags), which can be purchased anonymously online. They are available from individual sellers or retailers hosted on all major domestic e-commerce sites and mobile device apps (E-retailers, 2020), and often marketed without explicitly identifying their chemical contents to evade the oversight of regulatory authorities. Due to the ambiguous labelling and the strong oxidizing nature of sodium chlorate, it can be mistakenly used which caused a major explosion and fire in 2019 (DEMSP, 2019). To date, there have been only two public reports on the use of 'COD remover' in China. However, based on their product specifications (typically in 25-kg packages), the numbers of active sellers on e-commerce platforms, and the statistics on product transactions displayed by some retailers (E-retailers, 2020), the manufacturing and use of 'COD remover' may have created an underground industry, with some companies routinely using it for compliance purposes. One case report disclosed that the total amount of 'COD remover' used by a contractor of a municipal wastewater treatment plant had reached over 131,000 Kg (MEEC, 2021), while in another case a company received 2,000 Kg of 'COD remover' in a single delivery of the product (DEMSP, 2019).

These reports raise the question that whether such practices have *only* existed in China, given the fact that both COD measurement and the dichromate method are widely adopted by authorities as the standard protocols in wastewater compliance testing (BS, 1988; DIN, 1986; EPA, 1993; ISO, 1989, 2002; MEEC, 2017a, 2017b; UNE, 2002). After all, the chemistry is incredibly straightforward and the reagent itself is cheap, accessible, and highly effective in lowering COD measurements under the testing conditions. A further question needs to be raised that whether COD measurement has been the *only* target of chemical adulteration in wastewater compliance testing. The specific reactions and mechanisms involved in other compliance testing methods may also be exploited to manipulate the testing data. For instance, several standards and protocols use the iodometric method to measure the dissolved oxygen (DO) level in wastewater, including the ISO 5813 standard (ISO, 1983), the GB-7489 standard (MEEC, 1987), and the Winkler method specified by the US EPA (EPA, 1992). The addition of nitrite salts can increase DO measurements in the testing process by reacting with iodides and releasing nitric oxide and additional iodine, where sulfuric acid is added to dissolve manganese manganate precipitates in place and to form iodine (Lan et al., 2011). Moreover, cases of online monitoring devices being interfered to evade environmental regulation have also been reported. In 2017, a company in Zhejiang province, China, was found to intentionally feed lime-neutralized exhaust gas to reduce the concentrations of sulfur dioxide and nitrogen oxides measured in its emissions by an automatic sampling and online monitoring device (China Court, 2019). It is currently unknown whether there are other practices of chemical adulteration targeting the quality indicators used in current compliance testing of wastewater or exhaust gas emissions.

To rule out the presence of interfering agents in samples, it may be necessary to conduct a screening test prior to the standard testing protocols. In dichromate-based COD measurements, the presence of chlorates can be determined spectrophotometrically by ferric iron absorbance after their reduction by ferrous irons in sulfuric acid solutions (Prince, 1964). Where available, new modified testing methods or multiple testing methods that are unrelated in mechanisms may be specified by regulatory authorities for compliance testing. The use of improved methods or simultaneous use of two or more testing methods can improve the confidence in testing results. For instance, the modified Winkler method with sodium azide can suppress interferences by nitrites present in samples which would react with iodide in iodometric DO measurements (NEMI, 1997). Alternatively, unrelated testing methods may also be used to check the DO levels measured in the same wastewater samples by the iodometric method (ISO, 2012, 2014). In the long term, there is a need to develop more robust and adulteration-proof methods for wastewater and other environmental compliance testing.

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