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Alternative Method for Determination of the Chemical Oxygen Demand for Colloidal Polymeric Wastewater

N. S. Abuzaid, M. H. Al-Malack, A. H. El-Mubarak

Research Institute, King Fahd University of Petroleum and Minerals, P.O. Box 951, Dhahran, 31261, Saudi Arabia

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During the last several decades, vast industrial development has been experienced all over the world. While this development tremendously improved life standards, environmental problems and challenges that are posing hazards to living habitats have also evolved. Accordingly, increasing efforts are being practiced by environmental scientists and engineers in order to solve these problems. In this regard, different methods were developed for waste characterization which is the first step in approaching pollution related issues.

The complexity of many industrial wastewater effluents. where a matrix of pollutants with different concentrations co-exists, has necessitated the need for the use of general pollution parameters. Among these parameters are Total Organic Carbon (TOC), Biological Oxygen Demand (BOD), and Chemical Oxygen Demand (COD). While TOC analysis is valid for soluble organics (Schafferand et al. 1965) and BOD reflects the biodegradable part of the pollutants (Ruchhoft 1948), the COD analysis represents the total pollution load of most wastewater discharges (Moore et al. 1951). However, considering its wide range of error (USHEW-PHS 1963, the COD analysis can be considered costly and time consuming.

This study deals with a polymeric wastewater discharged by a chemical factory located in the Eastern Province of Saudi Arabia. The factory manufactures emulsion polymers such as homopolymers, copolymers, terpolymers, styrene acrylics, and pure acrylics. The discharged wastewater consists of very condensed colloidal polymers. Samples of the aforementioned wastewater are analyzed for COD on a daily basis in order to check for compliance with the standards of the regulatory authority for wastewater discharges to the existing treatment facility. It was found that ninety-nine percent of the wastewater total COD is contributed by the stable suspended colloidal polymers.

Turbidity analysis is conventionally conducted for river and lake waters and is used as a measure of clays and other natural suspended materials in these waters

Correspondence to: N. S. Abuzaid

(Baalsrud and Henriksen 1964) and (Talley et al. 1972). Due to its simplicity, the cost of turbidity analysis in terms of capital investment and operation is expected to be low.

The colloidal nature of the polymeric wastewater under study has motivated the authors to investigate the technical and economic feasibility of the turbidity test as an alternative to the COD analysis. In order to achieve this objective, samples are analyzed for COD and turbidity and the results of the two tests are related empirically. Additionally, economic feasibility of the proposed alternative is performed.

MATERIALS AND METHODS

A representative sample of the wastewater was collected and divided into two portions. One portion was filtered through 0.45 µm Millipore filter paper. The filtered and unfiltered portions of the wastewater were analyzed for COD in order to determine the soluble and suspended COD, respectively. The dichromate reflux method was adapted in the COD analysis following the procedure outlined by the Standard Methods (APHA 1980).

Different dilutions of the unfiltered sample were prepared so as to cover a suitable range of COD concentrations. Each dilution was analyzed for COD and turbidity. Turbidity was measured using Hach turbidometer model 2100N. Maximum effort was made to insure homogeneity of the wastewater either in the original sample or the diluted ones. Additionally, COD and turbidity analyses were conducted for six samples collected at different time intervals.

RESULTS AND DISCUSSION

The COD analysis of the filtered and unfiltered wastewater samples revealed that only 1% of the waste is in solution and the rest is suspended. It should be noted that if the percentage of soluble COD was high, there would have been no basis for the work because soluble COD does not reflect any turbidity.

The relationship between COD and turbidity for the colloidal polymeric wastewater under study is depicted in Figure 1. A simple empirical model that predicts the relationship between COD and turbidity data is developed. The model has the following form:

$$COD = k\left[Turbidity\right]^{c} \tag{1}$$

Equation 1 can be linearized as:

$$\ln COD = \ln k + c \ln Turbidity \tag{2}$$

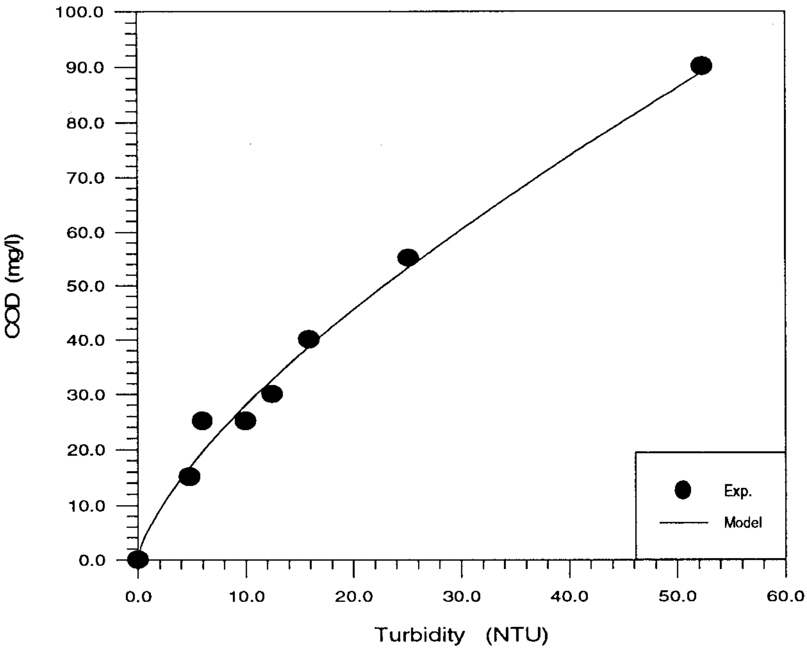
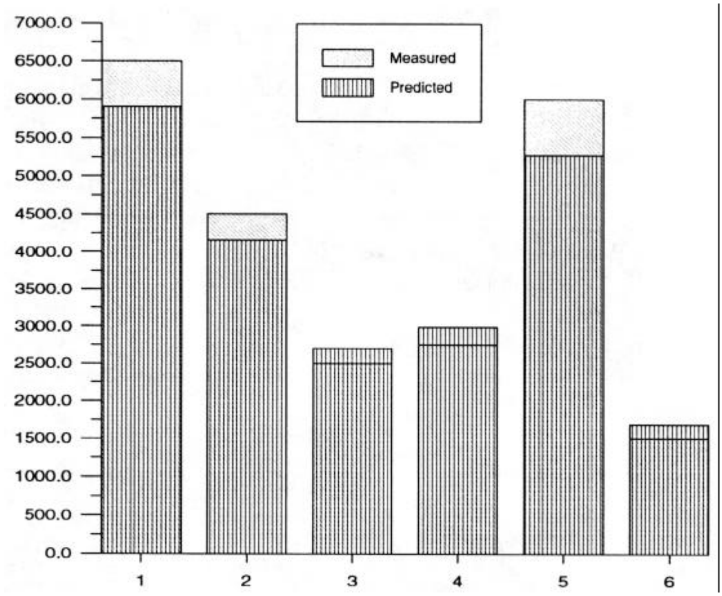


Figure 1. Relationship between COD and turbidity along with the model line of best fit.

where, k and c are model constants equal to 5.62 and 0.7, respectively. The strong predictive capability of the above mentioned relationship is obvious from the close fit it has for the experimental data as shown in Figure 1. Additionally, the coefficient of determination R^2 of the model was calculated and found very high (0.95). The use of the developed model is obvious; routine COD analysis for colloidal polymeric wastewater can be minimized by conducting the turbidity analysis and calculating the COD concentration using the aforementioned equation. However, the model should be periodically calibrated, particularly, when there are operational variations. Accordingly, it is recommended that the COD analysis should be occasionally conducted.

In order to test the validity of the model, it was used to predict the COD for six samples with known COD and turbidity values. Figure 2 presents the measured and predicted COD concentrations for the aforementioned samples. From the figure, it is clear that the good prediction of the model extended to samples other than those used for its development. Actually, the model underpredicts the highest three COD measurements with a deviation of 8-11% and overpredicts the lowest COD values with a deviation of 6-10%.

In order to investigate the economic feasibility of the above mentioned alternative, three main cost items are considered, i.e. equipment (capital investment), chemical reagents, and operation (labor). Since the equipment cost of a turbidometer and a COD setup are comparable, capital investment is factored out. Regarding the cost



Wastewater Samples

Figure 2. Measured and calculated COD concentrations.

of the COD reagents, the market price of a ready COD vial (equipped with the necessary reagents) of $ 1 will be used while the cost of ferrous ammonium sulfate titrant and its daily standardization reagents will be neglected. Practically, the turbidity analysis does not consume any reagents. The assumptions undertaken in the labor cost are; the possibility of analyzing six samples, simultaneously, the time for COD and turbidity measurements are 3 hours and 20 minutes, respectively, and the labor cost is $ 10/labor-hour. The costs of the COD and turbidity measurements were calculated using the aforementioned information as 6 and $ 0.55 per sample, respectively. The above cost analysis shows that 90% of the chemical analysis cost can be saved if the findings of this work are adapted. Reviewing the assumptions of the aforementioned cost analysis, it should be realized that this saving estimate is rather a conservative figure. Furthermore, the potential hazards of the chemical reagents associated with the COD analysis can be avoided.

The findings of this study can be extended to wastewater effluents similar to the investigated one. While the same approach can be adapted, different more suitable forms of relationships might be developed. However, it should be emphasized that this method is useful only for stable colloidal wastes where the constituents are insoluble polymeric oxidants that contribute both to chemical oxygen demand and turbidity.

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