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Catalytic thermal pre-treatments of sugar industry wastewater with metal oxides: Thermal treatment

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ABSTRACT

Water is essential to human health, economic growth, and environmentally sustainable development. Treating sugar industry effluent is one of the important tasks to save the nearby surrounding and recover the fresh water for industrial application. The goal of research work is to treat the sugar industry wastewater by metal catalyst using catalytic thermal treatment. The results show treatment with copper oxide 84.2% chemical oxygen demand and 89.6% color removal at 5 kg/m^3 catalysis mass loading, optimum pH5, operating temperature 85 °C and treatment time 9 h can be archives. The settling rate for 6 kg/m^3 mass loading has shown 55% clear liquid and 45% solid interface at 140 min of study. The cake resistance was 2.17×10^{13} (m/kg) and filter medium resistance 2.71×10^{9} m^{-1} for 5 kg/m^3 mass loading of copper oxide. The sludge obtained after thermolysis has high heating value and can be used as a fuel.

1. Introduction

Sugar is one of major product in India. According to the report, in 2015–16 approximately 168.5 million metrics tons sugar was produced in worldwide [14]. The sugar industry is based on agriculture which is playing a major role in strengthening the national economy and social development of a country [10]. The activities of sugar mills require a huge quantum of fresh water for milling processes and subsequently releasing of bulk effluent into the environment. Factories are consumsers of the huge volume of freshwater; wastewater contains a high level of contaminants such as suspended solids, organic and inorganic matter and chemicals [12]. Most chemicals used in sugar processing are toxic; if not well treated might ultimately find their course into the streams which make the poor quality of fresh water bodies [11]. This polluted water is utilized by a human for drinking, domestic, agriculture and industrial purposes. SIWW generally treated with the physicochemical and biological process [18]. The physicochemical method generates a large amount of sludge, which creates dumping problem [19]. The biological treatment process is slow and less efficient; it's only alternative for the treatment in small and medium scale industries [15]. In literature number of work was introduced to treat the sugarcane processing industry effluent [17,13]. These methods are not successful either due to economical way or management (space, manpower). Some alternative process, like thermolysis, is also available but it has been applied for other industry [20].

Thermolysis catalytic treatment involves in chemical decomposition of pollutant by means of temperature and metal salts catalyst like magnesium oxide (MnO), copper oxide (CuO), Zinc oxide (ZnO) etc. [3]. The reaction is usually endothermic as heat is required to break chemical bonds in the compound undergoing decomposition. The organics present in the wastewater either get polymerized/or decomposed into smaller molecules or get complexes with metal salts at temperatures in the range of ambient temperature to ~150 °C. The effects of temperature, pH, and autogenous pressure have been found to be the key parameters affecting the thermolysis with the settling and filtration characteristics of the precipitates. This process has been found to be suitable for the treatment of distillery effluent and significant COD reduction with the formation of the charred residue was observed [4]. The feasibility study of thermolysis has been also investigated for high strength organic wastewaters from pulp and paper mills [6], textile industry [8], petrochemical wastewater [20], etc.

The main objective of this research work is to treat the real sugarcane industry waste water by catalytic thermolysis processes. Effortlessly available metal salt has been used for catalyst preparation. The measure pollutant in wastewater like chemical oxygen demand and color was removed with different operating parameters like pH of sample, reaction time, experimental temperature and catalyst mass loading. Gravity settling and filtration were studied for sludge and slurry of effluent. The physicochemical characterization of sludge (solid-liquid) and catalyst have been also studied.

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2. Material and methods

2.1. Material

The industrial effluent was collected from Bhoramdev Sugar Industry Ltd. Kavardha (C.G.) India. It was preserved at 4 °C in the freezer untilled used, the physicochemical parameters are shown in Table 1. The laboratory grade chemical was used for experiment and analysis.

2.2. Experimental methods

A glass reactor was used for the thermolysis experiments at atmospheric pressure, shown in Fig. 1. The glass reactor having three-necked and capacity is 0.5 dm^3. The reactor placed a hot plate with magnetic equipped with a thermometer, vertical condenser and closed opening for sample collection. The temperature of the reaction mixture varies between 55 and 95 °C. A measured amount of wastewater and catalysis was taken in each run. Five milliliters of the sample were withdrawn at a definite interval of time and analyzed for its COD and color. The ambient temperature (T_0) to the treatment temperature (T_R) varied with the T_R. Therefore, the time of start of treatment was considered as the "zero time" when the T_R was attained after the preheating of the wastewater from T_0. The oven-dried residue was analyzed for its C, H, N, S and ash content. The initial pH of the wastewater was adjusted with by using either 0.1 N HCl or 1 M NaOH. The percentage removal of COD and color was calculated by Eq. (1).

$$Removal(\%) = \frac{(Ci - Cf) \times 100}{Ci} \quad (1)$$

Where,

Ci = Initial concentration (mg/l).

Cf = Finial concentration (after treatment; mg/l).

2.3. Catalyst preparation

Copper oxide (CuO), zinc oxide (ZnO), ferrous oxide (FeO) and magnesium oxide (MnO) were used as catalysts for thermolysis process. The metal oxide catalysts were obtained and prepared by precipitation from an aqueous solution of a metal salt followed by drying and calcination. The weighed samples were dissolved in distilled water and liquid ammonia was slowly added drop-wise to the metal salt solution while mixing the mixture vigorously. The resulting mixture was filtered and the retained precipitate on the filter was double-washed with distilled water to remove the traces of alkali present in the sample. The washed precipitate was carefully removed from the filter and dried in an oven at 105 °C for 18 h, which was followed by calcination at 350–400 °C for 4 h. The calcinations catalyst was ground in a laboratory grinder and sieved. The solid particles having an average size of 220 μm were used in the experiments.

Table 1
Physicochemical characteristics of sugar industry wastewater.

S. No	Characteristics	Before treatment
1	Color	Dark Yellow
2	pH	5.5
3	COD	3682
5	Phosphate	5.9
6	Protein	43
7	Total solid	1987
8	Suspended solid	540
9	Dissolved solid	1447
10	Chloride	50 mg/l
11	Hardness	900 mg/l

Except color and pH all values are in mg/dm^3.

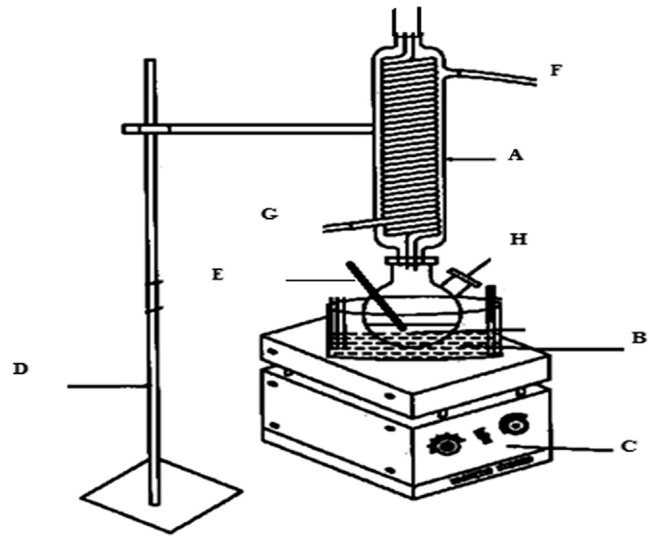

Fig. 1. Experimental setup of thermolysis process for sugar industry wastewater treatment (A) Condensers, (B) Heating mantle, (C) Magnetic stirrer, (D) Stand, (E) Thermometer, (F) Water inlet, (G) Water outlet, (H) Sample collection.

2.4. Analytical procedure

All the physicochemical parameter like COD, color, total solids, total dissolved solids, total suspended solid reduced carbohydrate, sulphate, chloride, etc., was determined per standard method of analysis (APHA, 1989). The color of the sample was measured in terms of the absorbance at λ = 420 nm using a UV–vis spectrophotometer (Model Lambda 35) from Perkin-Elmer Instruments, Switzerland. The residual organics in the treated effluent were analyzed by thermogravimetric analysis (TGA, SHIMADZU, DTG-60H). Settling has been done with 500 ml measuring cylinder and filtration study by using filter paper (What's man 42 No) and Buechner funnel.

3. Result and discussion

3.1. Effect of pH on COD and color reduction

The consequence of initial pH on thermal treatment of the sugar industries wastewater has been carried out with zinc oxide (ZnO), Ferrous Oxide (FeO), copper oxide (CuO), Manganese oxide (MnO) and without catalyst (WC) was studied in the AGR at atmospheric pressure and 75 °C. The results are shown in Fig. 2(a) and (b) all the experiments were carried out for a treatment time tr = 3 h, measured from zero time with the initial COD (COD_0) at 3682 mg/l, color 350PCU and the catalyst mass loading (C_w) at 4 kg/m^3. The initial pH was varied during the experiments in the range of 1–11. It was found that all the salt ZnO, FeO, MnO, and CuO show high reaction at the acidic solution as compared to basic nature of the solution. Maximum 62.3% COD and 65.5% color reduction were observed for copper oxide salt at pH5. Manganese oxide is shown 57.8% COD, 61.5% color reduction at pH 5, Zinc oxide 47% COD and 49.3% color reduction at pH 3, Ferrous oxide 41.4% COD and 46.1% color reductions at pH 5 and without catalysis used treated water shown 33% COD and 35.8% color reduction at pH7. The variation in percentage of chemical oxygen demand and color removal of sugar industry wastewater (SIWW) are may be due to combined effect of the active functional groups present in effluents and cata-