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ETHANOL REMOVAL USING ZINC AND COPPER METALLIC CATALYSTS FROM THE WASTE WATER OF ETHANOLIC GASOLINE PRODUCTION

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ABSTRACT

Nowadays, considering the ethanolic gasoline production growth worldwide, the necessity for eliminating the remaining ethanol in the waste water of the mentioned gasoline is noteworthy. In the present study, zinc and copper metallic catalyst was used to eliminate the by-produced ethanol. Different parameters such as: mass proportion of copper to zinc, total catalyst mass, pH, co-oxidative agent and temperature were optimized. After removal by catalyst, available ethanol in the samples was measured using gas chromatography (GC) instrument. In optimum conditions (mass proportion of copper to zinc 30:70%, 5grams of catalyst, 5.5 pH, temperature 20 ºC and contact time 60 minutes), the % removal was obtained about 85 %. The catalyst can be reused up to 5 times without significant property change. Results of this study have shown that the zinc and copper catalyst with hydrogen peroxide will make a proper way to removal of ethanol from the factory waste water producing ethanolic gasoline.

Keywords: Ethanol, Removal, Zinc and copper catalyst, Waste water

INTRODUCTION

The importance of petrol and gas industries in the civilized world is known to everyone. Although this industry, same as most production industries, makes lots of waste water. Considering this, the waste water for petrol industries consists of many organic and non-organic substances which can cause open water and earth pollutions (McNab et al., 1999; Houzhen et al., 2012). Gasoline has always been known as one of the most favored fuels among the petroleum derivatives which attempts on improving its structure's quality and efficacy, like raising the octane number resulting in better burning up, it has been one of the dimensions in research and scientific study for scientists all around the globe(Satge´ de Caroa, et al., 2001). One method to raise the octane number is to add different additives which Plumb (Pb) tetra-ethyl has been among the first and most popular additives (Perdih and Perdih, 2006; Wescott, 1936; Boyd, 1943). But after the intuition of lead's damaging effects on human health and environment and its incompatibility with catalyst convertors, now most countries have stopped adding lead to fuels and have replaced it with other additives. Nowadays ethanol is considered as the new biofuel and a replacement to fossil fuels. Ethanol is added to help raise the octane number as well as dramatically decrease gasoline use and is a proper substitute for harmful substances like MTBE (Benedict et al., 2003; Novak et al., 1985). But worldwide use of this biofuel has resulted in water, earth and atmosphere pollution and environmental destruction (Molson et al., 2002). By adding ethanol to gasoline in order to raise the octane number, it enters the atmosphere as a pollutant (Pimentel and Patzek, 2005) even though it doesn't seem toxic and dangerous in low concentrations, it

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could bring about very serious complications for individual health at over 100 ppb, such as: respiratory system irritation, negative effects on skin, eyes, including negative effects on sea life and other living creatures (Salge et al., 2005) ethanol eats metals especially in presence of water, so it progresses the galvanic reaction. Ethanol is an antiseptic and its presence in the waste water can destroy both useful and harmful bacteria (Barroso et al., 2012; Massa et al., 2004; Reitz et al., 2000). The global standard unit for ethanol in water is 100 ppb and according to US standards 50 ppb (Koester, 1999). In the late years researches have been conducted about ethanol oxidation in aquatic solutions using chemical oxidants. Ethanol oxidation by strong chemical oxidants such as nickel catalyst on alumina surface (Zambelli Mezalira et al., 2011), potassium permanganate $KMnO_4$ and sodium hypochlorite NaOCl (Bunyakan et al., 2005) and TiO_2 and Xenolith X13 (Ngadi and Jamaludin, 2005) were used.

In this study zinc and copper catalyst is used for the first time for ethanol oxidation in waste water sample. In the process of removal, different parameters such as mass proportion of copper to zinc, total catalyst mass, pH, oxidative agent and temperature were evaluated.

EXPERIMENTAL

Materials and Solvents Used

All reactants used in this project had high purity and were analytical grade special. Copper and zinc manufactured in industrial scales were used as powder with less than 20 µm diameters. Hydrogen peroxide 30% was introduced as the oxidative agent from Merck Industries. Acid Acetic, potassium hydroxide were also used from Merck industries to adjust pH. Stock solutions of 10000mgL^{-1}ethanol was derived from solving enough ethanol in deionized water (also from Merck) and all equipment used in different stages, were first washed with Nitric acid 5% and then twice with deionized water.

Devices

Shimadzo gas chromatography instrument model A14 made in Japan was used to determine ethanol concentration in samples. Impermeable to air Pyrex reactor, mechanical IKA shaker model Eurostar in order to make flow in the reactor, Mettler Ae 206 scale with 0.0001 grams preciseness and Mettler Toledo Instruments (Shanghai) was used to adjust pH.

Method

In order to optimize effective parameters on the removal rate, 5grams of zinc and copper metallic complex was added to reactor, water solution and ethanol with specific pH in each experiment. After certainty about the system being closed about air flow and precise connections of mechanical shaker with the device, the complex was agitated with the shaker for 120 minutes. Finally, catalysts were extracted by centrifuge at 2500 rpm in 5 minutes environment temperature. Remaining ethanol in the solution was measured with the GC device. To check the temperature effect, 25, 40 and 55 degrees centigrade and as for pH, 3, 5.5, 7, 9 and 11 were studied in the progress of ethanol removal. Oxidant effect on ethanol decomposition with optimized catalyst was evaluated. Different proportions of zinc and copper, total catalyst mass, time and temperature were also optimized.

RESULTS AND DISCUSSION

The Study of Copper to Zinc Mass Proportions Effect

Different proportions of copper and zinc to eliminate ethanol were studied. Figure 3-1 shows the effect of different parts of zinc and copper effect on ethanol removal; 70:30 proportion of copper to zinc showing the best removal in the experiment.

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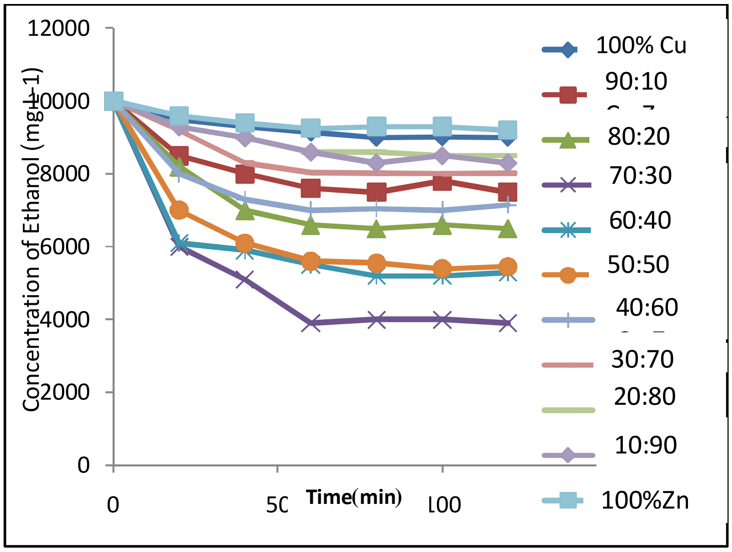

Figure 3-1.The study of different proportions of copper to zinc on ethanol Removal rate by catalyst (Concentration zero: 10000 ppm and pH=6, Contact time= 2 hrs., 10 grams catalyst, 250 mL solution)

The Study of Total Catalyst Mass Effect

Ethanol removal by catalyst results were studied in different masses (1-10 grams). Results are shown in Figure 3-2. According to Figure 3-2, the optimize quantity for catalyst was determined 5 grams. Use of higher masses is not advised because of high costs.

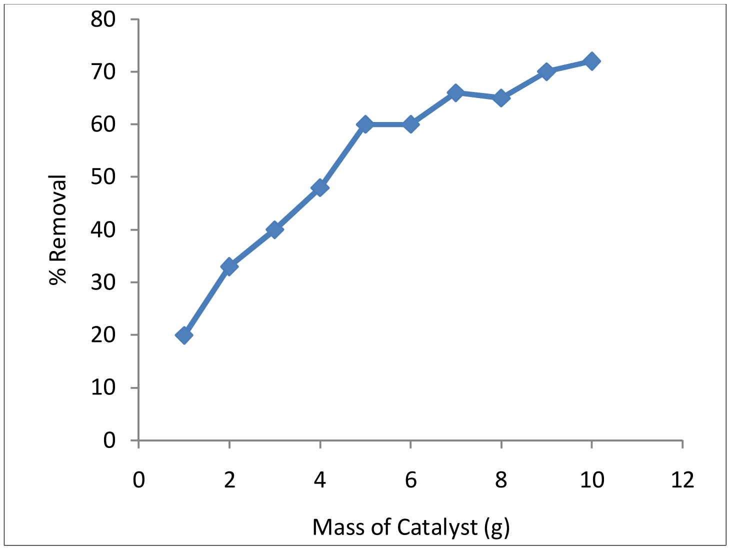

Figure 3-2. The study of total catalyst mass effect on ethanol removal rate by catalyst (Concentration zero: 10000 ppm and pH=6, contact time= 2 hrs, 5 grams catalyst, Optimized proportion 7:3 (copper: zinc), 250 mL solution).

The study of temperature effect

Ethanol removal by zinc and copper catalyst results in temperatures 25, 40 and 55 °C are shown in Figure 3-3. Most removal for catalyst takes place when the temperature is 25 °C. Actually, by raising the temperature, the catalyst efficacy decreases. Temperatures higher than 55 °C can cause breakdown in the reaction.

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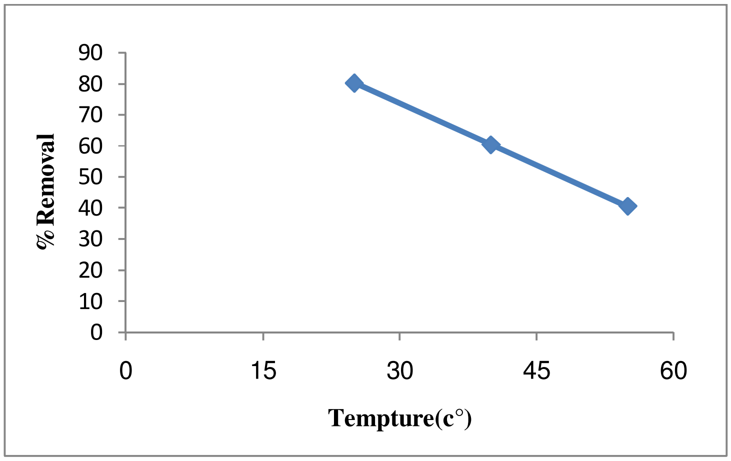

Figure 3-3. The study of temperature effect on ethanol removal rate by catalyst (Concentration zero: 10000 ppm and pH=6, contact time= 2 hrs, 5 grams catalyst, Optimized proportion 7:3 (copper: zinc), 250 mL solution)

The study of pH effect

In order to study pH, 3, 5.5, 7, 9 and 11 were chosen which results are shown in Figure 3-4. Best rate of removal happens in pH 5.5.

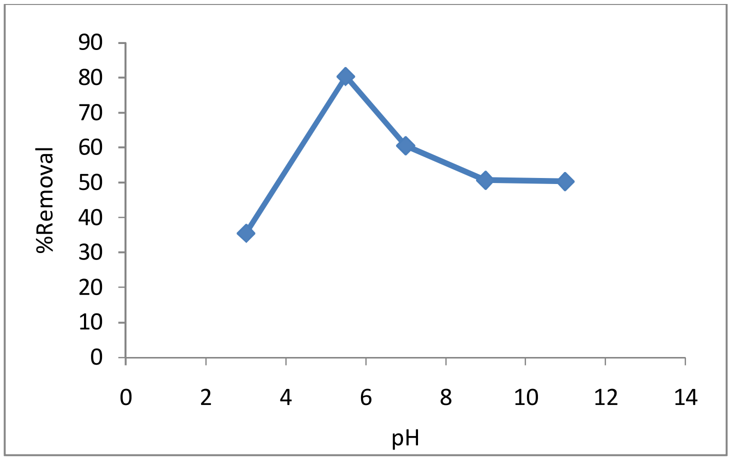

Figure 3-4. The study of pH effect on ethanol removal rate by catalyst. (Concentration zero: 10000 ppm, contact time= 2 hrs, 5 grams catalyst, Optimized proportion 7:3 (copper: zinc), 250 mL solution).

The Study of Oxidative Agent Effect

Among the usual oxidants, Hydrogen peroxide is the safest. In order to study the oxidant agent effect 20 ml of H_2O_2 0.5 M was used. Ethanol removal by catalyst, before and after adding the oxidant is shown in Figure 3-5. According to the Figure, after adding the oxidant agent rate of removal dramatically increases.

According to the Figure 3-5 removal rate increases as the contact time reaches 120 minutes and stays almost still afterwards. According to the Figure, it's clear that most of the removal has happened at 60 minutes time. In times closer to 120 minutes removal quantity difference has been little.

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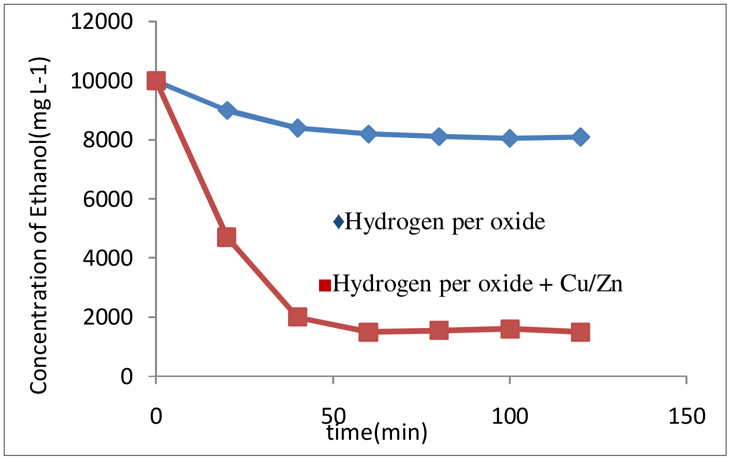

Figure 3-5. The study of oxidative agent effect on ethanol removal rate by catalyst. (Concentration zero: 10000 ppm and pH=6, contact time= 2 hrs, 5 grams catalyst, optimized proportion 7:3 (copper: zinc), 250 mL solution).

Usage in Waste Water Samples

Samples of ethanolic gasoline waste water were collected from Ahvaz Gas site. These samples were first filtered with 0.45µm layers and kept in Pyrex dishes. To study the real matrix effects in optimum conditions, water samples were spiked by 20 and 30mgL^{-1} ethanol solutions. Average results of the three tests are shown in Table 3-1.

Table 3-1. Recovery rate for 250 mL waste water samples in optimum conditions.

Samples	*Amount of added ethanol (mgL^{-1})*	*Amount of found ethanol (mgL^{-1})*	*Recovery (%)*
1	-	*20.53*±1.12	-
	30	*30.42*±1.35	99.00
	50	*50.34*±1.05	99.36
2	-	*21.05*±1.45	-
	30	*30.17*±1.78	91.20
	50	*49.15*±1.98	93.66
3	-	*20.48*±1.91	-
	30	*30.40*±1.55	99.20
	50	*50.20*±1.14	99.06

CONCLUSIONS

In this study metallic mix of copper and zinc was studied as ethanol eliminator catalyst and mass proportion effect of copper to zinc effect, total catalyst mass effect, pH effect, temperature effect and oxidative agent effect were determined during the removal process. According to the study it was made clear that copper and zinc catalyst has a high efficacy on eliminating ethanol. In this study the beneficial effect of hydrogen peroxide as oxidant was

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observed. Optimum contact time for ethanol removal was recorded 60 minutes. It was also noted that catalyst has the highest rate of ethanol removal at pH=5.5. Adding little amounts of catalyst increases the removal rate although higher amounts than the optimum 5 grams are not suggested because of no significant progress. Inexpensiveness, availability, ability to use for several times and convenience are the benefits of the mentioned catalyst for eliminating ethanol. This catalyst has proven very useful for eliminating ethanol from the gas site waste waters of ethanolic gasoline production.

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