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Full Length Research Paper

Removal of heavy metal from industrial wastewater using hydrogen peroxide

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The batch removal of heavy metals lead (Pb), zinc (Zn) and copper (Cu) from industrial wastewater effluent under different experimental conditions using hydrogen peroxide was investigated. Experimental results indicated that at pH 6.5, pre-treatment analysis gave the following values: Pb 57.63 mg/l, Zn 18.9 mg/l and Cu 13.9 mg/l. Removal of heavy metals was optimum at pH 7.6, a temperature of 30^{o}C, 1.5% hydrogen peroxide concentration and 60 min holding time, reducing the amounts of Pb, Zn and Cu by 83.5, 85.5 and 82.23%, respectively.

Keywords: Alum, effluent, hydrogen peroxide.

INTRODUCTION

One of the main causes of industrial pollution is the discharge of effluents containing heavy metals. Heavy metals can have serious effects on human and animal health. Beside the health effects, heavy metals are non-renewable resources. Therefore, effective recovery of heavy metals is as important as their removal from waste streams.

Disposal of industrial wastewater has always been a major environmental issue. Pollutants in industrial wastewater are almost invariably so toxic that wastewater has to be treated before its reuse or disposal in water bodies. Industrial processes generate wastewater containing heavy metal contaminants. Since most of heavy metals are non-degradable into non-toxic end products, their concentrations must be reduced to acceptable levels before discharging them into environment. Otherwise these could pose threats to public health and/or affect the aesthetic quality of potable water. According to World Health Organization (WHO) the metals of most immediate concern are chromium, zinc, iron, mercury and lead (WHO, 1984). Maximum allowed limits for contaminants in “treated” wastewater are enforced in developed and many developing countries.

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The treatment of contaminated waters is as diverse and complicated as the operation from which it comes. A number of conventional treatment technologies have been considered for treatment of wastewater contaminated with heavy metals. Previous investigations on the removal of heavy metals from wastewater (Howari and Garmoon, 2003; Shwarts and Ploethner, 1999; El-Awady and Sami, 1997) suggest that systems containing calcium in the form CaO or $CaCO_3$ and carbonates in general, are particularly effective in the removal of heavy metals from wastewater. Some of the conventional techniques for removal of metals from industrial wastewater include chemical precipitation, adsorption, solvent extraction, membrane separation, ion exchange, electrolytic techniques, coagulation/flotation, sedimentation, filtration, membrane process, biological process and chemical reaction (Blanco et al., 1999; Blanchard et al., 1984; Gloaguen and Morvan, 1997; Jeon et al., 2001; Kim et al., 1998; Lee et al., 1998; Mofa, 1995; Lujan et al., 1994; Gardea-Torresdey et al., 1996). Each method has its merits and limitations in application. Similarly, hydrogen peroxide (H_2O_2) has been used in different experiments to improve supply and oxidation rate of suspended and dissolved particles that cause pollution in such water effluent (Bami, 1989; Muganlinskii and Adeyinka, 1987; Adeyinka, 1996; Adeyinka and Rim-Rukeh, 1999; Chen et al., 1996).

Great importance has been attached to the treatment of industrial wastewater effluent since local and international authorities require that wastewaters from industries be treated and made to meet a set standard before it is discharged into the water bodies. Chemical treatment of industrial wastewater is preferable since industrial wastewaters are frequently complex, high in pollutant load and often containing materials toxic or resistant to the organisms on which biological processes depend. Also, chemical treatment systems are more predictable and inherently more subject to control by simple technique and chemicals are usually relatively tolerant to temperature changes.

In the chemical treatment of wastewater, the use of hydrogen peroxide has gained much popularity. H_2O_2 is a powerful oxidizer that looks like water in its appearance, chemical formula and reaction products. Despite its power, it is a versatile oxidant which is both safe and effective. It is one of the most powerful oxidizers known, stronger than chlorine, chlorine dioxide, and potassium permanganate, and through catalysis, H_2O_2 can be converted into hydroxyl radical (OH^-) with reactivity second only to fluorine. However, a review of the literature showed that very little investigation has been conducted to find out the effects of certain factors that contribute to H_2O_2 decomposition in the treatment of wastewater. Such factors include temperature, pH, H_2O_2 dose, etc. Hence, the objective of this work is to investigate the effect of H_2O_2 activated with Cu^{2+} on the removal of heavy metal ions in industrial wastewater effluent.

EXPERIMENTAL

Materials

Industrial effluent from a brewing industry in Nigeria was collected at the point of discharge into the stream. Materials used for sample collection were pretreated by washing the container with dilute hydrochloric acid and rinsed with distilled water. The containers were later dried in an oven for 1h at 110 ± 5°C and allowed to cool to ambient temperature. At the collection point, containers were rinsed with samples thrice and then filled with the sample, corked tightly and taken to the laboratory for treatment and analysis. All reagents used were of good analytical grade.

Wastewater sample preparation and analysis

10 ml of the wastewater sample was digested with 50 ml of conc. HNO_3 for 1 h. Thereafter, 40 ml of HCl was added at ratio 1:1 and digested for about 2 h on a hot plate magnetic stirrer. 1 ml of dilute HCl was further added to the sample and boiled for 1 h, filtered while hot with Whatman No 4 filter paper, washed with HCl and the volume made up to 100 ml with distilled water. The metals (Pb, Zn, and Cu) were determined using Atomic Absorption Spectrophotometer (AAS) Model: Phillip PU 9100 × with a hollow cathode lamp and a fuel rich flame (air acetylene). Sample was aspirated and the mean signal response recorded at each of the elements wavelength.

Wastewater treatment

Precipitation of metal ions: A sample of the wastewater was divided into six portions of equal volumes (500 ml), labeled A_1, A_2, A_3, A_4, A_5, and A_6. The first portion was further divided into five equal volumes (100 ml), labeled A_{11}, A_{12}, A_{13}, A_{14}, and A_{15} and each of the volume was treated with 50 ml of standard alum solution of varying concentrations (10, 20, 30, 40 and 50 ml/l). This was done to assess clarification and sedimentation by precipitation of complex metal ions that can be formed as a result of cation exchange reactions, especially Cu and Zn. Each of the five volumes (chemical and samples) was mixed slowly using a mechanical device for 30 min to create good sample-chemical contact. After this, they were filtered individually through a bed of activated clay and sodium ion exchange. The clarified effluents were collected and pH, Cu^{2+}, Pb^{2+} and Zn^{2+} were measured.

Study of the effect of H_2O_2 dose: The second experiment on the sample was done by dividing the sample, A_2 into five equal volumes labeled A_{21}, A_{22}, A_{23}, A_{24} and A_{25} and treating each of the samples with alum concentration with maximum percentage removal in A_1 with the addition of 50 ml of standard volume of H_2O_2 solution of 30% concentration. Each of the five portions of the sample was then treated with the H_2O_2 (0.5, 1.0, 1.5, 2.0 and 2.5%) volume of the effluent. The liquid content of sample-H_2O_2 mixture was agitated for 30 min with a mechanical device for effective sample-chemical contact after which it was filtered through a bed of activated clay followed by sodium ion exchange. Clarified effluents were collected and analysed for parameters as in above.

Study of contact time effect: The third portion of the effluent, A_3 was divided into five equal volumes, A_{31}, A_{32}, A_{33}, A_{34} and A_{35}. Using H_2O_2 concentration with maximum percentage removal in treatment two above, the effect of contact time was determined by keeping the concentration of H_2O_2 constant and agitating each of the samples for 20, 40, 60, 80 and 100 min in order to ensure effective sample-chemical contact. After this, the content was filtered as in treatment one and the resulting clarified effluent was analysed.

Study of temperature effect: The fourth portion of the effluent, A_4 was also divided into five equal volumes A_{41}, A_{42}, A_{43}, A_{44} and A_{45}. Using the H_2O_2 concentration in treatment two, time with maximum percentage removal in treatment three, the samples were agitated at various temperatures; 10, 20, 30, 40, and 50°C, respectively. After this, the content was filtered as in treatment one and the resulting clarified effluent was analysed.

Study of pH effect: A similar procedure was carried out for the fifth portion of the sample, A_{51}, A_{52}, A_{53}, A_{54}, and A_{55} and using H_2O_2 concentration with maximum percentage removal in treatment two and pH of 4, 6, 8, 10 and 12 , respectively, for each of the portions. For effective effluent-chemical contact, the mixture was agitated using the best contact time in treatment three. The content was filtered as in treatment one and the resulting clarified effluent was analysed.

Study of the effect H_2O_2 activated with $CuSO_4$: The last portion of the effluent, A_6 was divided into five equal volumes, A_{61}, A_{62}, A_{63}, A_{64} and A_{65} respectively. Using H_2O_2 concentration with maximum percentage removal in treatment two, the effect of H_2O_2 activated with $CuSO_4$ (15, 25, 35, 45 and 55 ml) on treatment method was determined by using contact time with maximum percentage removal in treatment three; temperature with maximum percentage removal and pH in treatments four and five, respectively, and agitat-

ing each of the samples in order to ensure effective sample-chemical contact. After this, the content was filtered and the resulting clarified effluent was analysed.

RESULTS AND DISCUSSION

Sample treatment was carried out using alum for clarification while hydrogen peroxide and copper (II) sulphate were used as treatment reagent. Interesting results were obtained using H_2O_2 activated with $CuSO_4$. The physico-chemical analysis of the wastewater is presented in Table 1.

Table 1. Characterization of the effluent wastewater.

Parameter	Concentration (mg/l)
pH	6.5
Pb^{2+}	57.63
Zn^{2+}	18.90
Cu^{2+}	13.90

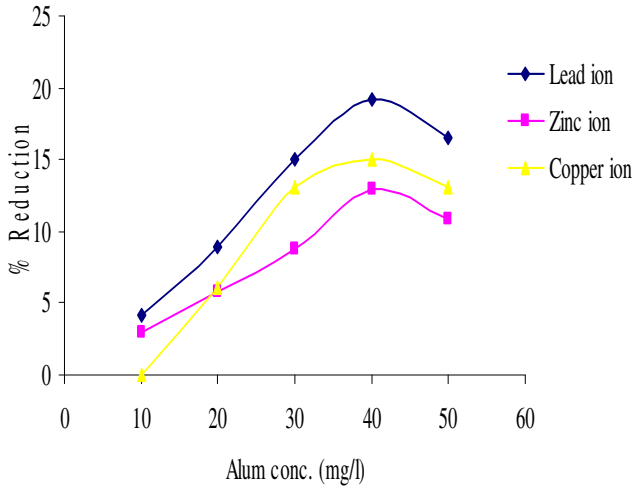

Figure 1. Quality of effluents obtained from alum clarification and treatment in bed of activated clay.

Analysis after precipitation of metal ions

Figure 1 depicts the result obtained from treatment one in which the alum-clarified sample was passed through a bed of activated clay and sodium-ion exchange. The results are expressed in term of the percentages of metal ion removal from the water sample. The sodium-ion exchange was used in all the experiments to remove alum traces that may be dissolved in the effluent during clarification, as well as to remove other ions that may cause impurities in the water (Adeyinka and Rim-Rukeh, 1999). Analyses of the effluent showed a reasonable reduction of Pb^{2+} from 57.63 to 46.58 mg/l (19.17% removal)

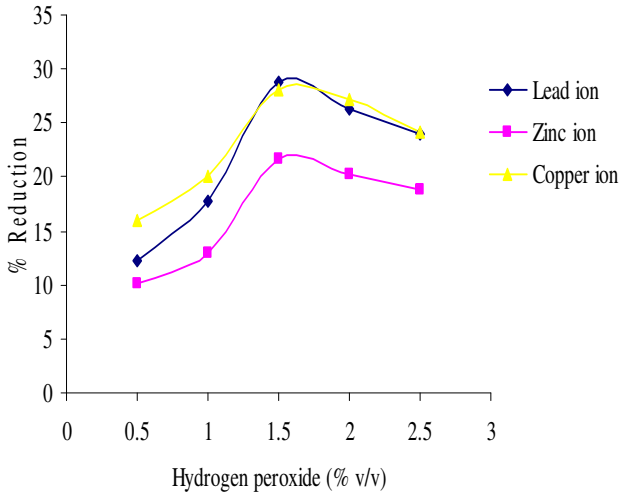

Figure 2. Quality of effluents obtained from hydrogen peroxide and treatment in a bed of activated clay.

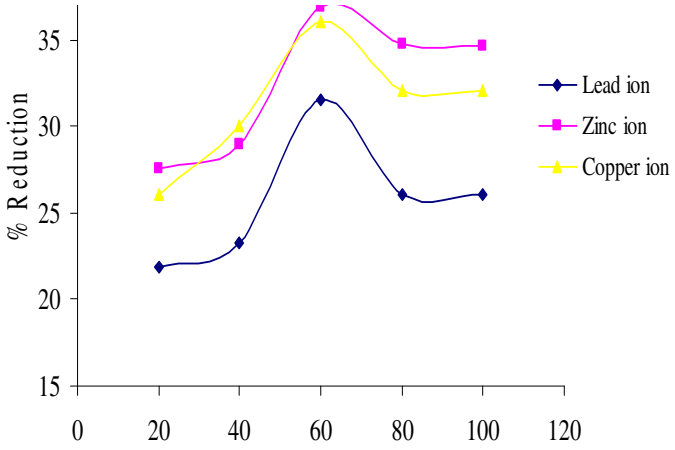

Figure 3. Effect of contact time on quality of effluents obtained.

while Zn^{2+} was reduced from 18.9 to 16.44 mg/l giving a 13.02% removal. Cu^{2+} was reduced from 13.90 mg/l to 11.81mg/l (15.04% removal).

Influence of hydrogen peroxide

Figure 2 shows the results of the influence of H_2O_2 dose on wastewater effluents. Analysis of the treatment and the results showed a considerable reduction of Pb^{2+} (1.5% H_2O_2 conc.) from 57.63 to 41.05 mg/l (28.77% removal), while Zn^{2+} was reduced from18.9 to 14.79 mg/l (21.75% removal). Cu^{2+} was reduced from 13.9 to 10 mg/l (28.06% removal).

Influence of contact time

Figure 3 represents the percent removal of Pb^{2+}, Zn^{2+} and Cu^{2+} at different contact times. The results showed that

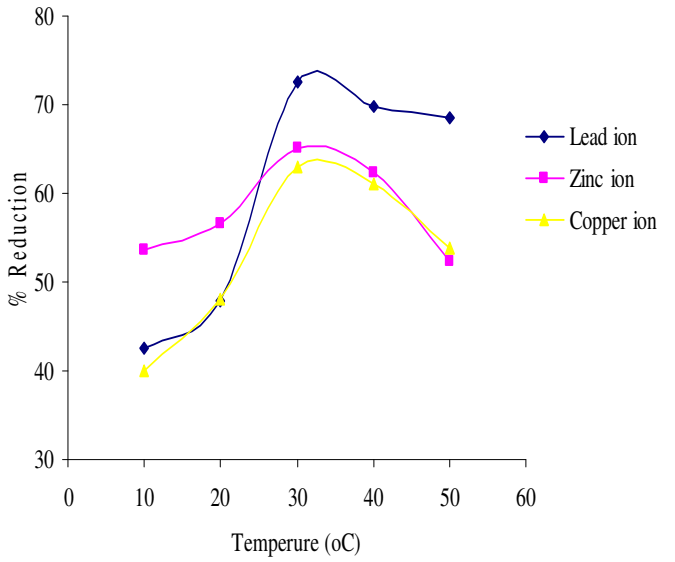

Figure 4. Effect of temperature on quality of effluents obtained.

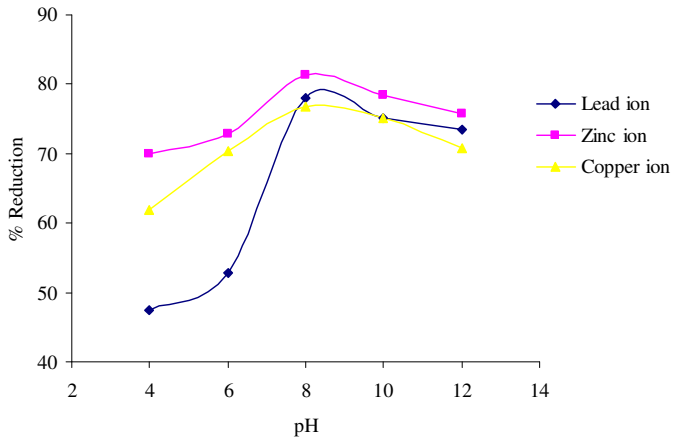

Figure 5. Effect of pH on quality of effluent obtained.

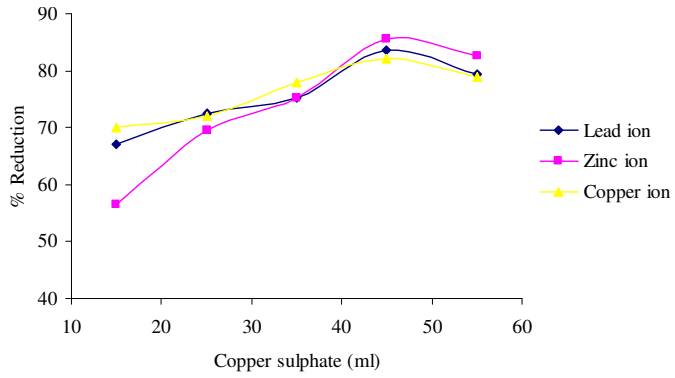

Figure 6. Effect of hydrogen peroxide activated with copper sulphate on quality of effluent obtained.

Pb^{2+} removal was more than 31.51% at a contact time of 60 min, while Zn^{2+} and Cu^{2+} removal are 36.93 and 36.04% respectively.

Influence of temperature

Figure 4 indicates the influence of temperature on the percent removal of Pb^{2+}, Zn^{2+} and Cu^{2+}. It was observed that maximum removal occurred at the 30°C with Pb^{2+} reduced from 57.63 to 15.79 mg/l (72.60%); Zn^{2+} from 18.9mg/l to 6.58 mg/l (65.19%) and Cu^{2+} from 13.9 mg/l to 5.14 mg/l (63.02%). This is due to the fact that decomposition of H_2O_2 is favoured by increasing temperature (Bishop, 1968). The reduction in percent removal after this temperature may be possible due to the abundance of OH^- ions causing increased hindrance to diffusion of metal ions.

Influence of pH

Figure 5 depicts the effect of pH on percent removal of determined physico-chemical properties. The result shows that maximum removal occurs at pH of 7.6, with Pb^{2+} reduced from 57.63 to 12.69 mg/l (77.98% removal); Zn^{2+} was reduced from 18.9 to 3.54 mg/l (81.27%) and Cu^{2+} from 13.9 to 3.24 mg/l (76.70%). The result shows that with the increase in the pH of the wastewater sample, the extent of removal increases. But after pH 8, there is a decrease in the removal of metal ions. This decrease may be due to the formation of soluble hydroxyl complexes. According to Baes and Mesmer (1973), as the sample pH increases, the onset of the metal hydrolysis and the precipitation began at pH > 6. The hydrolysis of cations occurs by the replacement of metal ligands in the inner co-ordination sphere with the hydroxyl groups (Gau et al., 1985). This replacement occurs after the removal of the outer hydration of metal cat ions. This tremendous increase in percent reduction of metal ions with increase in pH up to 8 is due to the fact that decomposition of H_2O_2 is favoured by increasing pH especially at pH 6 – 8 (Bishop, 1968).

Influence of Cu^{2+}

Figure 6 represents the effect of Cu^{2+} on treatment method. It was observed that the extent of percent removal decreased with increasing concentration of Cu^{2+}. Analysis of the result, showed that Cu^{2+} (45 ml) activated H_2O_2 synergetically leading to Pb^{2+} reduction from 57.63 to 9.47 mg/l (83.57%) with a correlation coefficient of 0.8928, Zn^{2+} from 18.9 to 2.74 mg/l (85.5%) with a correlation coefficient of 0.9323, whilst Cu^{2+} was reduced from 13.9 to 2.47 mg/l (82.23%) with a correlation coefficient of 0.8774. This treatment showed improved effluents quality

and higher oxidative ability. Decomposition of H_2O_2 to give H_2O and O_2 is highly favoured. Increasing contamination especially with transition metals activates (catalytic activity) the breaking down of H_2O_2 molecule to H_2O and O_2. The results showed higher effectiveness relative to other treatments formulated for the effluents treatment.

Conclusion

In the present study, the removal of heavy metals, Pb, Zn and Cu using H_2O_2 was found to be effective. The process efficiency was enhanced by activating the H_2O_2 with Cu^{2+}, increasing the breaking down of H_2O_2 molecule to H_2O and O_2. The results obtained show that hydrogen peroxide can be used effectively in the removal of heavy metal ions from industrial wastewaters.

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