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Removal of COD and Colour from Sanitary Landfill Leachate by using Coagulation – Fenton's Process

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ABSTRACT: This study investigated two methods for the removal of COD and colour from sanitary landfill leachates. The first method involved the use of coagulation/flocculation process using $FeCl_3$ as a conventional coagulant and $Ca(OH)_2$ as base-precipitant. The second method involved integration of Fenton's reagent into the coagulation/flocculation process. Concentration of $FeCl_3$ that reduced chemical oxygen demand (COD), and color by 37 and 62% is 1000mg/l. Fenton-coagulation flocculation process reduced the COD and color of the leachates by 88 and 98% respectively. The optimum conditions for the effectiveness of Fenton's reagent, namely temperature, pH, H_2O_2 and coagulant dose were studied. @JASEM

Landfill leachate from municipal solid waste landfill sites are often defined as hazardous and heavily polluted wastewaters. The leachates may contain a large amount of organic matter (both biodegradable and biorefractory carbon), ammonia-nitrogen, heavy metals, chlorinated organic and inorganic salts (Wang *et al.,* 2002). The discharge of landfill leachate can lead to serious environmental problems as they may percolate through soils and sub soils, causing extensive pollution of ground and surface waters if they are not properly treated and safely disposed (Tatsi *et al.,* 2003). Landfill leachate treatment by several methods namely coagulation - flocculation (Tatsi *et al.,* 2003; Amokrane *et al.,* 1997); coagulation - photo oxidation (Wang *et al;* 2002); nanofiltration (Marttinen *et. al,* 2002); biological treatment and combined physico-chemical-nanofiltration process (Treboutet, *et al.* 2001) have been reported. $FeCl_3$ is a widely used coagulant and it has been used for the removal of organic matter in landfill leachates (Tatsi *et al*., 2003) and industrial wastewater (Peres *et al.,* 2004; Amoo *et al.,* 2004).

Fenton's reagent (hydrogen peroxide in the presence of a ferrous salt) has been used for the treatment of both organic and inorganic substances under laboratory conditions as well as real effluents from different resources like chemical manufacturers, refinery and fuel terminals, engine and metal cleaning etc. (Gogate and pandit, 2004). The process is based on the formation of reactive oxidizing species, able to efficiently degrade the pollutants of the wastewater stream (Bossman *et al.,* 1998; Pignatello *et al.,* 1999). In the oxidation system, three reactive species are involved; two of them involve the presence of hydroxyl radicals (classical Fenton's chemistry) in either 'free' or 'caged' form, whereas third oxidant has been postulated to be aquo or organo-complexes of the high valence iron, the ferryl ion (Gogate and Pandit, 2004). The oxidation system can be effectively used for the destruction of toxic wastes and non-biodegradable effluents to render them more suitable for a secondary biological treatment (Perez *et al.,* 2002 Martinez *et al.,* 2003; Peres *et al.,* 2004).

Therefore, in the first phase of the present work, a coagulation/flocculation method is applied for COD and color removals from the landfill leachate, whereas, the second phase involves coagulation - Fenton process for COD and color removal from the landfill leachate. The specific aim of this work was to study the relative effects of different operational schemes such as temperature, pH value, concentration of H_2O_2 and coagulant dose.

MATERIALS AND METHODS

Leachate sampling: The leachate was collected from Aboru Landfill site (Lagos, Nigeria). Characteristics of the leachate sample are as shown in Table 1.

Table 1. Characteristics of landfill leachate sample

pH	7.9
Conductivity (μscm^{-1})	27.2
BODs (mg/l)	2560
COD (mg/l)	5420
Color (pt unit Co)	6900
Turbidity (NTU)	315
TDS (g/l)	15.2
TSS (g/l)	0.76

Sample analyses: The samples were taken to the laboratory in sealed plastic barrels, stored at -4^{O}C before analyses. The initial pH of the sample was determined by a pH meter, the COD and color were

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determined following standard methods for the examination of water and wastewater (APHA – AWWA-WEF, 1995).

EXPERIMENTAL PROCEDURES

Effect of coagulant dose on coagulation: Different concentrations such 100, 250, 500, 750 or 1000 mg $FeCl_3$ was added to a 1000 ml leachate sample. After rapid mixing for 5 min at 200 rpm and slow mixing for 55 min at 60 rpm, the sample was withdrawn by using a plastic syringe from a point about 2 cm below the top of liquid level at the beaker in order to determine the COD and color, so that the effect of coagulant dose on coagulation could be studied. For the purpose of coagulation, pH was adjusted to 8.5 by addition of $Ca(OH)_2$.

*Effect of hydrogen peroxide dosage on the coagulation - Fenton process***:** In the Fenton-Coagulation/flocculation experiment, a dose of H_2O_2 (0.1 to 2 M) was added to coagulation - flocculation process in glass reactors, after 120 min, supernatant was sampled to determine COD and color, so that effect of different dose of H_2O_2 could be studied.

*Effect of temperature on the coagulation – Fenton process***:** Temperature was varied among 25,35, 40, 45 and 50^0C in glass reactor after addition of H_2O_2. After 120 min, supernatant is sampled to determine COD and color so that effect of temperature on the treatment could be studied.

Effect of ph on the efficiency of coagulation-Fenton process: pH was adjusted (2.5, 3, 4 and 5) after addition of H_2O_2. After 120 min, supernatant is sampled to determine COD and color, so that effect of pH on the treatment could be studied.

RESULTS AND DISCUSSION

Effect of coagulant dose on coagulation: The effect of different doses of $FeCl_3$ on the removal of COD and color by coagulation is shown in Fig. 1.

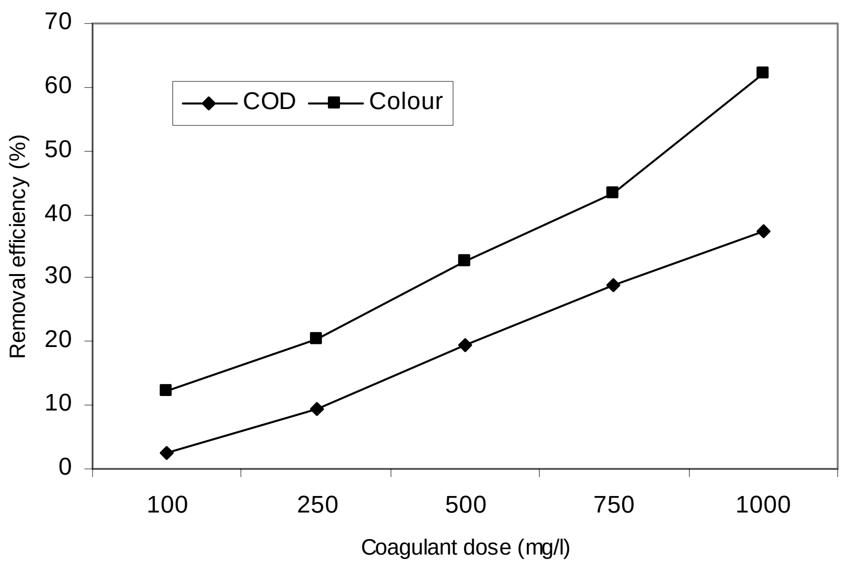

Fig. 1: Effect of coagulant dose on the removal of COD and colour in the leachate

The removal of COD and color increased with increasing concentration of $FeCl_3$. The highest values (37 and 62%) of COD and color respectively were obtained using a Fe^{3+} dosage of 1000mg/l.

Effect of hydrogen peroxide dosage on the coagulation - fenton process: The effect of H_2O_2 on the removal of COD and color during coagulation-Fenton process is as shown in Fig. 2.

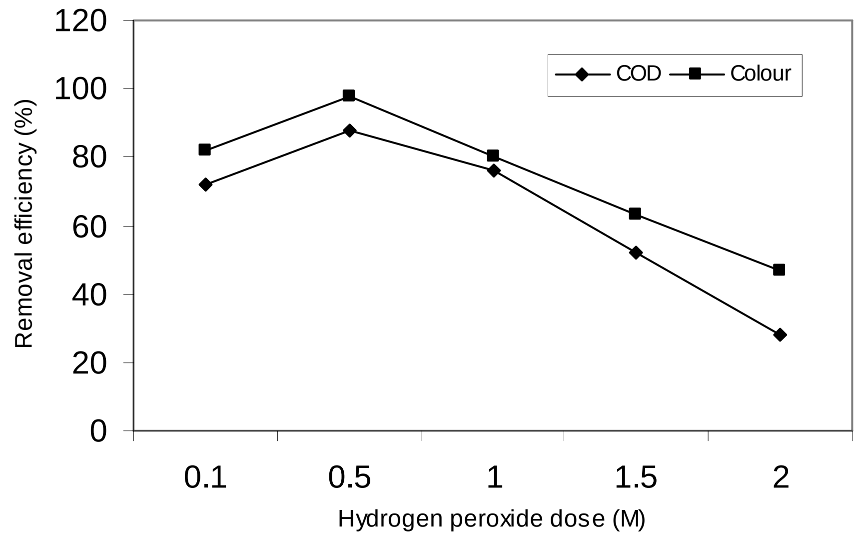

Fig. 2: Effect of H_2O_2 dosage on coagulant-Fenton process for the removal of COD and color in the leachate

The dosage of H_2O_2 was varied among 0.1, 0.5, 1.0, 1.5 and 2 M, increasing the dosage of H_2O_2 from 0.1 to 0.5 M increases the enhancement of removal of COD and color in the leachate sample; this finding is in line with the reports of Lin *et al.,* 1999; Kang and Hwang 2000. However, at greater than or equal to 1.0 M dosage of H_2O_2, the removal efficiency of COD reduced. Residual H_2O_2 may have contributed to COD. It can be concluded at this point that the dosage of H_2O_2 that enhances coagulation-Fenton process is in the range of 0.1 to 0.5 M. Higher dosage of H_2O_2 may be harmful to microorganisms thus, creating problem to overall degradation efficiency in the subsequent biological treatment .

Effect of pH on the efficiency of coagulation-Fenton process: pH has been observed to significantly affect degradation of COD and reduction of color. Others (Lin and Lo, 1997; Kang and Wang 2000) observed similar results. The effect of pH on the removal of COD and color is as shown in Fig. 3.

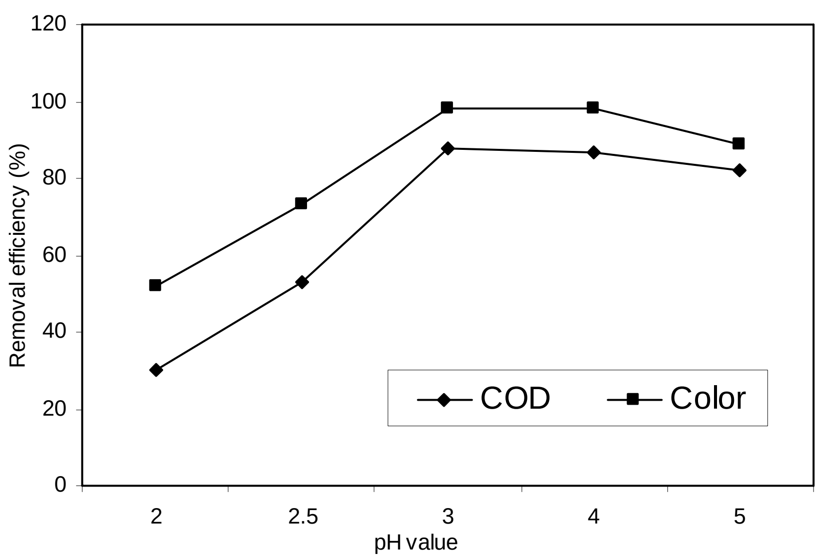

Fig.3: Effect of pH on the efficacy of coagulation – fenton process for the removal of COD and Color in the leachate

The pH of the system was varied among 2, 2.5, 3, 4 and 5. In the present work, the recommended pH for this system is in the range 2.5 to 4. At pH < 2.5 there was reduction in the removal efficiency of COD. This may be due to the formation of Fe (II) complex which reacts more slowly with H_2O_2 and this, produces fewer amounts of hydroxyl radicals thereby reducing the efficiency of the process. At pH > 4, the removal efficiency also reduced this may be due to decrease of the free iron species in the reacting system which in turn may be due to formation of Fe (II) complex. Kwon *et al.*, (1999) reported decrease in the oxidation potential of $HO^{\cdot}$ radical with an increase in the pH.

Effect of temperature on coagulation-Fenton's process: Temperature only enhanced the removal of COD very slightly and as such its effect was neglected in all the experiments.

Sequel to this, temperature does not need to be considered in the optimization of Fenton's reaction for the treatment of the leachate studied.

*Effect of fecl$_3$ on the coagulation-Fenton process***:** The effect of different dosages of $FeCl_3$ on the coagulation-Fenton process is shown in Fig. 4.

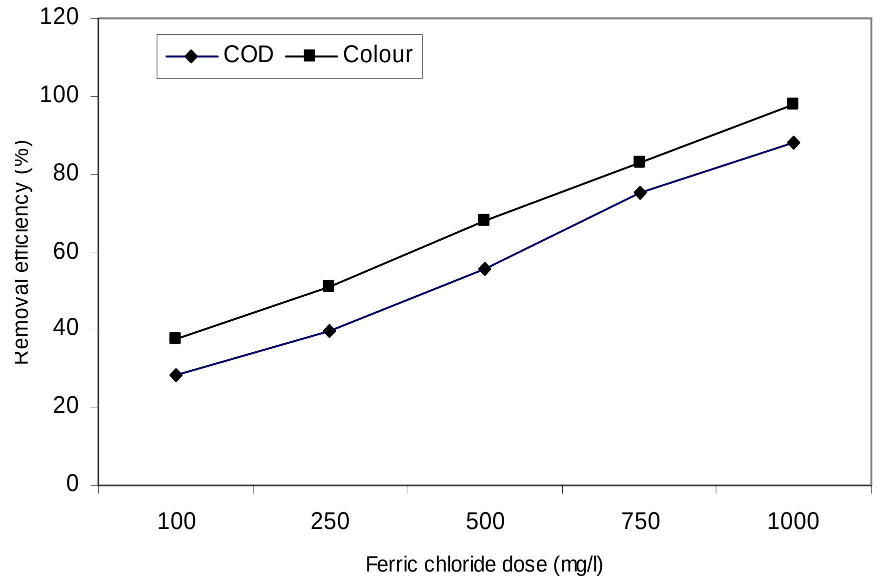

Fig. 4: Effect of different dosages of $FeCl_3$ on the coagulation-Fenton process

Increasing the concentration of $FeCl_3$ up to 1000mg/l increases removal efficiency of COD and color. The reaction of the iron salt (Fe^{2+} or Fe^{3+}) with H_2O_2 in Fenton system produces hydroxyl radicals as shown in reaction (1):

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^-$$

The produced Fe^{3+} can react with H_2O_2 to produce hydroperoxyl radical

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + H_2O \ + \ H^+$$

Lower doses of $FeCl_3$ favor the reaction of the Fe^{2+} with the H_2O_2 to generate hydroxyl radicals $OH^{\cdot}$ that are more reactive than hydroperoxyl ($HO^{\cdot}_2$) radicals (reaction 1). These in turn favor removal efficiency of COD and color from the leachate. Higher doses of $FeCl_3$, for a given (H_2O_2) concentration, accelerates the rate of decomposition of the H_2O_2 by reaction (2) to produce hydroperoxyl radicals ($HO^{\cdot}_2$) that are less reactive than $OH^{\cdot}$. Increase in the ferrous ions lead to an increase in the unused quantity of iron salts; which contributed to an increase in the total dissolved solids (TDS) content of the leachate. (Gogate and Pandit, 2004) Highest removal efficiencies of 88 and 98% COD and color respectively were obtained with 1000 mg $FeCl_3$.

Conclusion: Coagulation-Fenton process was used to treat landfill leachate collected from Aboru sanitary landfill site (Lagos, Nigeria). Results of the experiments revealed the following: 1000mg$FeCl_3$ reduces COD and color by 37 and 62% respectively. The pH range of 3-4 was found to be effective for the coagulation-Fenton process. Increasing dosage of H_2O_2 from 0.1 to 0.5 M increases the enhancement of removal of contaminants. Higher dosage can act as scavengers for the generated hydroxyl radicals that are needed by ferryl ion to maintain Fenton's reaction. Temperature effect on the removal of COD from the leachate during Fenton's reaction process was negligible. 1000mg $FeCl_3$ enhances efficient removal of COD and color in the coagulation-Fenton process by 88 and 98% respectively. Increasing $FeCl_3$ above 1500 mg leads to an increase in the unused quantity of iron salt which contributes to increase in the TDS content of the landfill leachate.

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