

Removal of Heavy Metals from Pharmaceutical Industrial Wastewater Effluent by Combination of Adsorption and Chemical Precipitation Methods

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Abstract: The removal of heavy metals from our environment especially industrial effluents is now shifting from the use of conventional adsorbents to the use of chemical precipitation. The presence of heavy metals in the environment is a major concern because of their toxicity, bioaccumulating tendency, and threat to human life and the environment. The main objective of this research is to study the effectiveness of the combination of hydrogen peroxide and activated bentonite clay in the removal of heavy metal ions from pharmaceutical industrial effluent. About 13.790 mg/l of Fe, 1.650 mg/l of Zn and 2.000 mg/l of Ni were detected in the digested sample and batch removal of heavy metals such as Fe, Zn and Ni from industrial wastewater effluent under different experimental conditions using hydrogen peroxide as precipitating agent in combination with activated bentonite clay as adsorbent. Appreciable differences in the level of heavy metals concentration were observed based on pH effect. The result shows higher effectiveness relatives to other treatments formulated for the effluent treatment such as Alum precipitation effect, effect of hydrogen peroxide concentration dose, contact time effect and temperature effect. Removal of heavy metals in effluent was optimum at pH 10 for zinc (Zn) and nickel (Ni) and at pH 8 for iron (Fe), at temperature of 50°C, 0.75% hydrogen peroxide concentration dose and 100 mins holding time, reducing the amounts from 13.790 to 1.436 mg/l of Fe, while 1.650 to 0.127 mg/l of Zn and 2.000 to 0.115 mg/l of Ni respectively. The percentage differences in concentration for the heavy metals removal in industrial wastewater are as follows: Fe (89.58%), Zn (92.30%) and Ni (94.22%). The result showed high level of Zn and Ni generated from this pharmaceutical industry is above 1 mg/l FEPA and WHO standard but only Fe showed low level concentration compared to 20 mg/l FEPA and WHO standard in this study. This study reveals the need for enforcing adequate effluent treatment methods before their discharge to surface water to reduce their potential environmental hazards.

Keywords: Heavy Metals, Pharmaceutical Effluent, Hydrogen Peroxide, Activated Bentonite Clay

1. Introduction

Environmental protection and rational use of natural resources and other industrial raw materials has become a very important sphere of mankind's advancement in the 20th century. Mankind's demand for resources and raw materials has increased the ecological and economic contradictions in the industries (Sen and Chakrabaty., 2009). This wide spread industrialization in urban areas has drastically reduced land area for waste disposal. Disposal of untreated industrial and domestic wastes into the environment affects both soil and

ground water quality. Soil and streams have been used for multivarious purposes including waste disposal.

The industrial effluents consist of organic compounds along with inorganic complexes and other non-biodegradable substances. These pollutants not only alter the quality of ground water and soil but also pose serious problems threats to public health and/or affect the aesthetic quality of potable water. (Karthikeyan et al., 2010). According to World Health Organization (WHO), the metals of most immediate concern are chromium, zinc, iron, mercury and lead (WHO, 2010) and Maximum allowed limits for contaminants in "treated" wastewater are enforced in developed and many developing

countries (Deng *et al.*, 2003). The effluents discharge by different industries contain a high range of physical and chemical parameter like Temperature, pH, Conductivity, Hardness, Alkalinity, Oxygen demand, Total suspended solid, Nitrate, Nitrite, Cations and Anions. The Environmental contamination with heavy metals is a consequence of technological and industrial advances (Davydova 2005; Wong *et al.*, 2006). The principal problem associated with this anthropogenic contamination is toxicity against all living organisms, in particular, humans (Chapman *et al.* 2003; Florea and Büsselberg 2006; Sharma and Agrawal 2005). "Heavy metals" is a general collective term applying to the group of metals with an atomic density greater than 6gcm^3 . It is widely recognized and usually applied to the elements such as lead (Pb), chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), cadmium (Cd), and zinc (Zn) etc which are commonly associated with pollution and toxicity problems (Morais *et al.*, 2012). Some of the elements in this group are required by most living organisms in small for normal healthy growth, but excess concentration causes toxicity. Heavy metals cannot be degraded or destroyed and they enter our bodies via food, drinking, water and air. As trace elements, some heavy metals are essential to maintain the metabolism of the human body but at higher concentration they can lead to poisoning. Heavy metals are dangerous because they tend to bioaccumulate and bioconcentrate in living tissue and biomagnify as it moves through the trophic levels (Sridhara *et al.*, 2008). It is therefore, essential and important to remove or reduce the presence of these inorganic contaminants in order to diminish the possibility of uptake by plants, animals, and humans and eventual accumulation in the food chain and also to prevent them from contaminating surface and groundwater by dissolution or dispersion (Kabata-Pendias 2001; McLaughlin *et al.* 2000). To restore the heavy metal contaminated soil, tremendous expenses and time are required for complete remediation. 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 Calcium oxide or Calcium trioxocarbonate (iv) 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, Rai *et al.*, 2002). Each method has its merits and limitations in application but 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. 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^\cdot) with reactivity second only to fluorine. Likewise adsorption has been recognized as a potential technology for the removal of heavy metals and other pollutants from waste water in comparison to other physical, chemical and biological methods available for the treatment of wastewater (Abasi *et al.*, 2011), adsorption is the most preferred technique due to simple and flexible design and easy operation. The adsorption process may generate little or toxic pollutants and involve low initial capital and operating costs (Y. S. Ho., 2004, Crini, G., 2006, Abdel *et al.*, 2007). Bentonite is a common natural cation exchanger (Espantaleón *et al.*, 2003) and According to (Ozcan and Ozcan., 2004), the specific BET surface area and surface acidity, lowest pore volume and lowest average pore size can be easily and significantly increased by acid activation, therefore both natural bentonite and acid activated bentonite were of high significant compare to all other adsorbents available. However, from a review of literature shows that there is little available information on the combination of adsorption and chemical precipitation in removal of heavy metals from industrial effluents. Hence the objective of this work is to investigate the effect of hydrogen peroxide (H_2O_2) in combination with activated bentonite clay on the removal of heavy metal ions in industrial wastewater effluent.

2. Preparation of Adsorbent

Bentonite is absorbent Aluminium phyllosilicate generally impure clay consisting mostly of Montmorillonite and related clay minerals of the smectite group, which are characterized by a large surface area per unit of weight and high Cation Exchange Capacity (CEC), (Ozcan and Ozcan., 2004). The bentonite clay sample was dispersed in the distilled water, the dispersed clay was stirred and allowed to settle and the upper layer which consists of particles was sieved off. The lower layer was continuously stirred and sieved off until it become free from suspended particles. The dispersed clay was allowed to settle for 24hrs to allow the sedimentation process The top layer was collected via decantation and the remainder was washed with distilled water, allowed to settle for 24hrs (for further sedimentation) and decanted to collect the top layer. The sol (prepared bentonite clay) was dried under the sun for several days,

pulverized and sieved using 100 μ m mesh size to obtain clay of less than 100 μ m particle size. 150g of prepared bentonite clay was mixed with 200ml of 2M HNO₃ solution for acid activation of clay in a 1000ml beaker. The mixture was stirred and diluted with distilled water up to 800ml mark of the beaker and was allowed to settle for 24hrs. The aqueous phase was gently decanted. The acid treated or modified bentonite clay was placed in a crucible and oven dried for 3hrs at a temperature of 180-200°C. The dried activated bentonite clay was pulverized and sieved using 100 μ m mesh size.

3. Materials and Methods

3.1. Materials

All glassware was calibrated before use and all reagents used were analytical grade obtained from Adfolak Nigeria Enterprise, Ibadan, Nigeria. All glassware and containers used were washed with acid water and distilled water before used to avoid cross contamination. Distilled water was used throughout the study.

3.2. Methods

Industrial effluent from a pharmaceutical industry in Ibadan, Nigeria was collected at the point of discharge into the stream after the production time. 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 (Model LR-271C) for 2hours at 120 \pm 3°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. The longitude and latitude were taken as N 07^o 23' 59.50" and E 003^o 58' 0.40" at the sample point collectively. The pH and temperature of the wastewater sample at the collection point were 10.40 and 30°C respectively using (Mudder 0.01 readout accuracy digital pocket pen type, Backlit LCD.0.00-14.00 pH meter).

3.2.1. Wastewater Sample Digestion and Analysis

Wet digestion was employed using 250ml of the wastewater sample with 10ml of concentrated HNO₃ for 3hrs till the volume of the reaction mixture was reduced to about 30ml on a hot plate magnetic stirrer (2 LTR Capacity with 220/110 Volt). It was then filtered while hot with Whatman No 4 filter paper, and the volume made up to 50ml with distilled water. The metals in the digested sample were determined using flame Atomic Absorption Spectrophotometer (AAS) (Model: buck scientific VPG210) 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 heavy metals concentration in mg/l such as iron, zinc, copper, lead, cobalt, nickel, manganese, chromium and cadmium in the sample was determined but only iron, zinc and nickel were detected from the wastewater.

3.2.2. Wastewater Treatment

A. Precipitation of metal ions using Alum Solution: A sample of the wastewater was divided into five portions of equal volumes (250ml) labelled A₁, A₂, A₃, A₄ and A₅. The first portion was further divided into five equal volumes (50ml) labelled A₁₁, A₁₂, A₁₃, A₁₄, and A₁₅ and each of the volume was treated with 25ml of standard alum solution of varying volume (5, 10, 15, 20 and 25) ml. This was done to assess clarification and sedimentation by precipitation of complex ions. Each of the five volumes (chemical and samples) was mixed slowly using a mechanical device for 30mins to create good sample-chemical contact. After this, they were filtered individually through a bed of 5g of activated bentonite clay. The clarified effluent were collected and analysed; Zn, Fe, and Ni were measured. Blank sample was prepared by adding Standard Alum solution and distilled water, and the resulting solution was analysed.

B. Study of the effect of H₂O₂ dose: The second experiment on the sample was done by dividing the sample, A₂ into five equal volumes labelled A₂₁, A₂₂, A₂₃, A₂₄ and A₂₅ and treating each of the samples with Alum concentration with maximum percentage removal in wastewater treatment A above with the addition of 25ml of standard volume of H₂O₂ solution of 30% concentration to oxidize heavy metals ion present, oxidize both organic and inorganic pollutants present and to improve their adsorption, filtration, or precipitation from wastewaters. Each of the five portions of the sample was then treated with the H₂O₂ (0.25, 0.50, 0.75, 1.0 and 1.25)% volume of the effluent. The liquid content of sample-H₂O₂ mixture was agitated for 30mins with a mechanical device for effective sample-chemical contact after which it was filtered individually through a bed of 5g of activated bentonite clay. Clarified effluents were collected and analysed for Zn, Fe, and Ni parameters.

C Study of contact time effect: The third portion of the effluent, A₃ was divided into five equal volumes, A₃₁, A₃₂, A₃₃, A₃₄ and A₃₅. Using H₂O₂ concentration with maximum percentage removal in wastewater treatment B above, the effect of contact time was determined by keeping the concentration of H₂O₂ constant and agitating each of the samples for 20, 40, 60, 80 and 100 mins in order to ensure effective sample-chemical contact. After this, the content was filtered individually through a bed of 5g of activated bentonite clay and the resulting clarified effluent was analysed for Zn, Fe, and Ni parameters.

D Study of temperature effect: The fourth portion of the effluent, A₄ was also divided into five equal volumes A₄₁, A₄₂, A₄₃, A₄₄ and A₄₅. Using maximum percentage removal of H₂O₂ concentration in treatment 3.2.2. B above, time with maximum percentage removal in wastewater treatment C above, samples were agitated at various temperatures; 10, 20, 30, 40 and 50°C respectively. Increasing the temperature of the reaction will almost always make the reaction go faster in removing of the heavy metals present in the effluent and help in decomposition of the H₂O₂. After this, the content was filtered individually through a bed of 5g of activated bentonite clay and the resulting clarified effluent was

analysed for Zn, Fe, and Ni parameters.

E Study of pH effect: A similar procedure was carried out for the fifth portion of the sample, A₅₁, A₅₂, A₅₃, A₅₄, and A₅₅ and using H₂O₂ concentration with maximum percentage removal in wastewater treatment B above and pH of 4, 6, 8, 10 and 12 respectively, for each of the portions in order to increase hydrolysis and precipitation of the heavy metals present in the effluent. For effective effluent-chemical contact, the mixture was agitated using the best contact time in wastewater treatment D above. The content was filtered individually through a bed of 5g of activated bentonite clay

$$\text{percentage reduction (\% reduction) of heavy metals} = \frac{a - b}{a} \times 100 \%$$

Sample treatment was carried out using Alum solution for clarification while hydrogen peroxide and activated bentonite clay were used as treatment reagent.

Environmental standards for effluent limitation of World Health Organisation (WHO) and Federal Environmental Protection Agency (FEPA) are presented in Tab. 2 together with the results of the digestion analysis.

Tab. 1. Result of Analysis of the Chemical used (Blank Sample).

Chemicals	Fe(mg/l)	Zn(mg/l)	Ni(mg/l)
Alum	nd	nd	nd
Distilled water	nd	nd	nd

nd: not detected.

Tab. 2. Physicochemical Analysis of Industrial Effluent after digestion compare to FEPA and WHO Effluent Maximum Permissible Limit.

Parameters	Concentration	Maximum Permissible	Maximum Permissible
	(mg/l)	Limit FEPA (mg/l)	Limit WHO (mg/l)
pH	1.80		
Fe	13.790	20	15
Zn	1.650	<1	<1
Ni	2.000	<1	<1

Source: FEPA., 2003.

4.1. Distribution of Heavy Metals Present in the Industrial Effluent Sample

The concentration of selected heavy metals in the industrial effluent are represented in Tab. 2 above showing the analysis obtained from the digested sample using Flame Atomic Absorption Spectrophotometer (AAS) analysis and pH of the industrial effluent sample after digestion. Generally amount of heavy metals decrease from iron which had a distinct high concentration, followed by nickel to zinc which was the least metal in the study but the concentration levels of chromium, copper, lead, cobalt and cadmium were not detected in the digested effluent sample.

4.2. Analysis of Wastewater Sample After Precipitation of Metal Ion Using Alum Solution

The result obtained from wastewater treatment A in which the Alum-clarified sample at various concentrations was

and the resulting clarified effluent was analysed for Zn, Fe, and Ni parameters.

4. Result and Discussion

Formula used in calculating percentage reduction of heavy metals in the wastewater;

Conc. of wastewater after digestion = a

Conc. of wastewater after digestion + treatment of wastewater with activated bentonite clay & H₂O₂ = b

Therefore,

passed through a bed of activated bentonite clay. The results are expressed in term of the percentages of metal ion removal from the wastewater sample. The alum was used in all the experiments as coagulant aids to remove the impurities that may be dissolved or present in the effluent, as well as to remove other ions that may cause impurities in the water (Adeyinka and Rim-Rukeh., 1999). In this study, the concentration of the Alum was varied from 5 - 25ml, on increasing the Alum concentration; this caused increase in the removal efficiency of the metals. At 20ml Alum concentration, analysis of the effluent showed a reasonable reduction given Fe²⁺ from 13.790 to 11.720 mg/l (15.01% removal), while Zn²⁺ was reduced from 1.650 to 1.381 mg/l (16.25% removal) and Ni²⁺ was reduced from 2.000 to 1.656 mg/l (17.20% removal). Ni²⁺ ions show a dramatical highest percentage removal due its highest structure density of (8.908 g/cm³) comparing to Fe²⁺ (7.874 g/cm³) and Zn²⁺ (7.14 g/cm³) ion present in the effluent. Current and Structure density determines the coagulant dosage rate and the floc growth resulting in a faster removal of pollutants (Holt et al., 2002). From this study, it was found that Alum addition enhances coagulation process which is more effective at the end when the concentration is higher than at the beginning of the operation when the concentration is low which help in removing of heavy metals as they were passed through activated bentonite clay. The same observation was reported by other workers (Santarsiero et al., 1998; Tatsi et al., 2003 and Zhu et al., 2004).

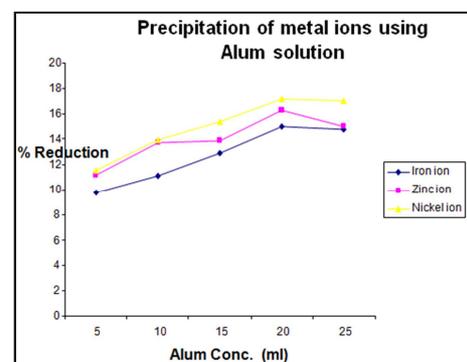


Fig. 1. Percentage reduction of effluent obtained from Alum Precipitation and treatment in bed of activate bentonite Clay.

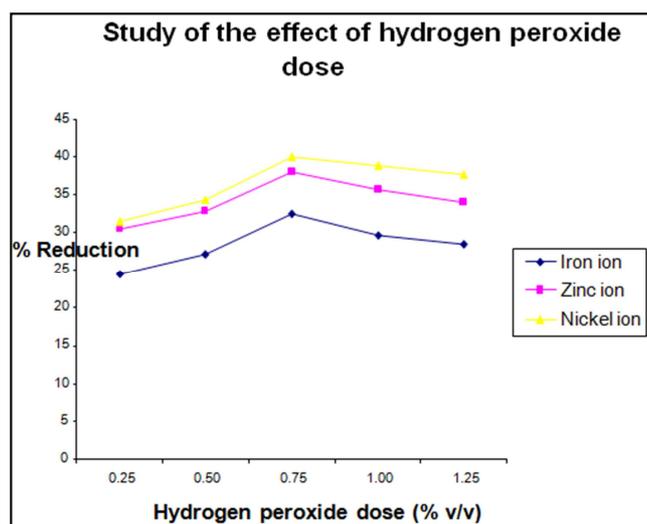


Fig. 2. Percentage reduction of effluent obtained from hydrogen peroxide and treatment in bed of activated Bentonite Clay.

4.3. Analysis of Wastewater Sample Using Hydrogen Peroxide

Fig. 2. shows the result obtained from wastewater treatment B in which 20ml of Alum-clarified sample was influence by H_2O_2 dose at various concentrations on wastewater effluents and then passed through a bed of activated bentonite clay. The results are expressed in term of the percentage of metal ion removal from the wastewater sample. H_2O_2 was used in the experiment to oxidize heavy metals ion present, oxidize both organic and inorganic pollutants present and to improve rate of their adsorption, filtration, or precipitation from wastewaters. H_2O_2 decomposes to give H_2O and O_2 which form hydroxide with the heavy metals present in the effluent sample. Analysis of the treatment and the results shows that when the concentration of hydrogen peroxide dose was increased from 0.75 - 1.25ml, there is decrease in the percentage removal of the three heavy metals present in the effluent due to the availability of different side reaction, Reduction of free Fe^{2+} , Zn^{2+} , Ni^{2+} ions, this condition results to the decrease in percentage removal of the three heavy metals present in the effluent which later result to more of hydroxyl ion (OH^-) in solution reacting with excess hydroxyl ion (OH^-) from the decomposition of hydrogen peroxide and form hydrogen peroxide in the solution.

When the concentration of hydrogen peroxide increases above 0.75ml, there is decrease in the absorption of the metals with the adsorbent (Rodrigez M. et al., 2002) but when the concentration of hydrogen peroxide dose was increased from 0.25 - 0.75ml, there is dramatic increase in the percentage removal of all the three heavy metals present in the effluent due to more increase in ionic interaction between the metal and the hydrogen peroxide with activated bentonite clay (adsorbent) forming soluble metals which can be recovered as insoluble metal hydroxide such as $Zn(OH)_2$, $Fe(OH)_3$, $Ni(OH)_2$ (Bauer R., Fallman H., 1997; Pignatello et al., 1999). From the study, on increasing the concentration dose of hydrogen peroxide to 0.75ml showing best reduction

of Fe^{2+} from 13.790 to 9.311 mg/l (32.48% removal), while Zn^{2+} was reduced from 1.650 to 1.024 mg/l (37.92% removal) and Ni^{2+} was reduced from 2.000 to 1.201 mg/l (39.95% removal). Ni^{2+} has highest percentage removal on treating hydrogen peroxide due to its high solubility in hydrogen peroxide than Fe^{2+} and Zn^{2+} ions.

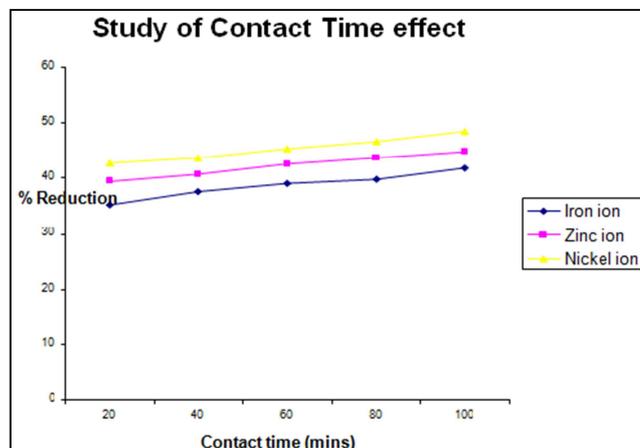


Fig. 3. Percentage reduction of effluent obtained from contact time and treatment in bed of activated Bentonite Clay.

4.4. Analysis of Wastewater Sample Based on Contact Time Effect

Fig. 3. shows the results obtained from wastewater treatment C in which 20ml/l of Alum-clarified sample was influence by H_2O_2 dose at 0.75% concentration of the volume of wastewater sample showing maximum percentage removal in wastewater treatment B and agitating each of the samples for 20, 40, 60, 80 and 100 mins in order to ensure effective sample-chemical contact. After this, the content was filtered through a bed of activated bentonite clay and the resulting clarified effluent was analysed. Fig. 3, obviously shows that uptake of Fe^{2+} , Zn^{2+} and Ni^{2+} ions by the method used with activated bentonite clay was rapid with contact time effect. Initially, the rate of removal of Fe^{2+} , Zn^{2+} and Ni^{2+} ions was low because the active site on H_2O_2 and activated bentonite clay were of small time contact with the metal ions and this leads to low concentration of adsorption, but increase of contact time increases the uptake rate of the metal ions present in the effluent due high contact time between the metal ions and the active site on H_2O_2 and activated bentonite clay (Mureithi et al., 2012). Removal efficiency increased with an increase in contact time and this can be explained by the affinity of the adsorbents towards metal ions (Ramana et al., 2002). The increased uptake of all the metal ions with contact time can be due to the decreased mass transfer coefficient of the diffusion controlled reaction between the adsorbent and the metal ion (Bhattacharya A. K, et al., 2006). As contact time increases, the percentage of heavy metal removal increases drastically from 20 - 100mins showing that Fe^{2+} , Zn^{2+} and Ni^{2+} ions has high affinity for the adsorbent used. However, analysis of the treatment and the results showed the best reduction at a contact time of 100 mins of

Fe^{2+} from 13.790 to 8.043 mg/l (41.67% removal), while Zn^{2+} was reduced from 1.650 to 0.910 mg/l (44.82% removal) and Ni^{2+} was reduced from 2.000 to 1.028 mg/l (48.59% removal). Therefore, 100 mins contact time is recommended for Fe, Zn and Ni removal from wastewater by hydrogen peroxide.

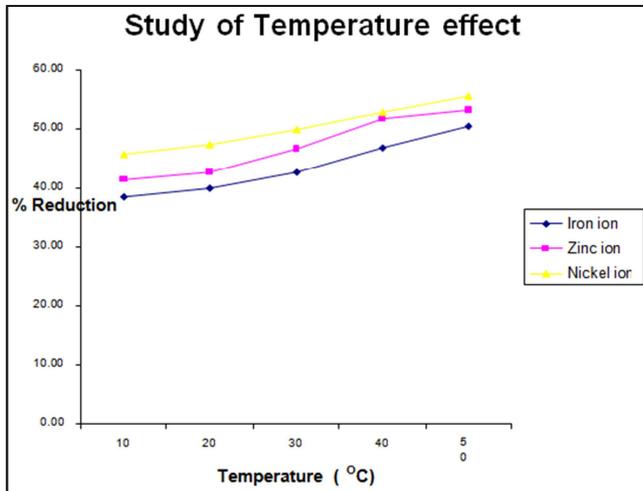


Fig. 4. Percentage reduction of effluent obtained from Temperature and treatment in bed of activated Bentonite Clay.

4.5. Analysis of Wastewater Sample Based on Temperature Effect

Fig. 4. shows the results obtained from wastewater treatment D in which 20ml/l of Alum-clarified sample was influenced by H_2O_2 dose at 0.75% concentration of the volume of wastewater sample showing maximum percentage removal in wastewater treatment B and agitating each of the samples for 100 mins at various temperatures; 10, 20, 30, 40, and 50°C, respectively to make the reaction go faster in removing of the heavy metals present in the effluent and help in decomposition of the H_2O_2 . After this, the content was filtered through bed of activated bentonite clay, and the resulting effluent was analysed. Increase in temperature brings about increase in adsorption rate as shown in Fig. 4. As the temperature increases, the percentage of heavy metal removal increases rapidly from 10 - 50°C respectively. Removal efficiency increases with an increase in temperature and this can be explained due to the fact that decomposition of H_2O_2 is favoured by increasing temperature (K. Akhtar, 2009). Analysis of the treatment and the result show a good reduction at 50°C of temperature to give Fe^{2+} from 13.790 to 6.820 mg/l (50.54% removal), while Zn^{2+} was reduced from 1.650 to 0.771 mg/l (53.24% removal) and Ni^{2+} was reduced from 2.000 to 0.866 mg/l (55.68% removal). The increase in percentage removal of Fe^{2+} , Zn^{2+} and Ni^{2+} ion at this temperature (50°C) may be possible due to the abundance of OH^- ions causing increased hindrance to diffusion of metal ions (Ozer and Ozer, 2003). Increase in temperature increases adsorption for Fe^{2+} , Zn^{2+} and Ni^{2+} . This result indicates that the chemical precipitation and adsorption of Fe^{2+} , Zn^{2+} and Ni^{2+} ions is endothermic in nature (Jaman et al., 2009).

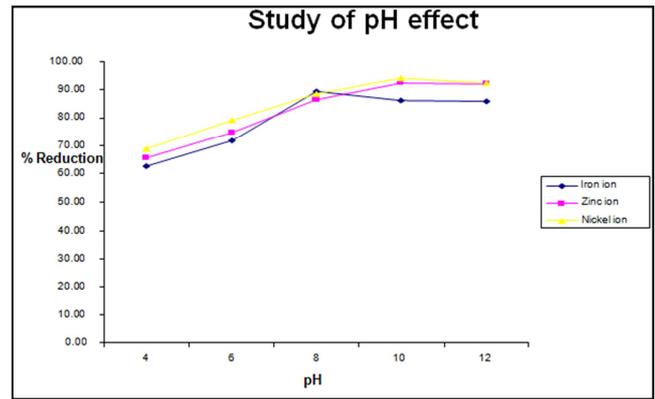


Fig. 5. Percentage reduction of effluent obtained from pH and treatment in bed of activated Bentonite Clay.

4.6. Analysis of Wastewater Sample Based on PH Effect

Fig. 5. shows the result obtained from wastewater treatment E in which 20ml/l of Alum-clarified sample was influenced by H_2O_2 dose at 0.75% concentration of the volume of wastewater sample showing maximum percentage removal in treatment B and agitating each of the samples for 100 mins at temperatures of 50°C, and taken the pH of each sample at pH of 4, 6, 8, 10 and 12, respectively in order to increase hydrolysis and precipitation of the heavy metals present in the effluent. After this, the content was filtered through bed of activated bentonite clay, and the resulting effluent was analysed. The effect of pH on the adsorption of Fe^{2+} , Zn^{2+} and Ni^{2+} is presented in Fig. 5. pH is an important factor in adsorption chemistry of aqueous metal ions because of its influence on aqueous metal ion speciation and surface characteristics of adsorbent (Shiundu et al., 2012). The pH of the aqueous solution is an important operational parameter in the adsorption process because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction (Amuda, O. S et al., 2007). The active sites on an adsorbent can either be protonated or deprotonated depending on the pH while at the same time the adsorbate speciation in solution depends on the pH too.

Generally, metal ions are more soluble at lower pH values and this enhances their adsorption as previously reported by Olayinka et al. (2009). At a pH value of 4, low metal ion uptake is observed for Fe^{2+} , Zn^{2+} and Ni^{2+} ions. The use of pH 4 may result in the competitive adsorption of the hydrogen ion (H^+) and three metal ions on the hydrogen peroxide and the activated bentonite clay surface. At pH 4, the adsorbent is positively charged and hence offers repulsive force to approaching the metal ions. However, more Fe^{2+} , Zn^{2+} and Ni^{2+} ions uptake is observed as the pH increases which is due to the fact that at high pH values, Fe^{2+} , Zn^{2+} and Ni^{2+} ions still have a net positive charge but exist as FeOH^+ , ZnOH^+ and NiOH^+ while most active sites on the adsorbent are deprotonated. This leads to net attractive force that is responsible for high Fe, Zn and Ni removal from solution in the alkaline pH range. This result shows that with increase in pH of wastewater from 8-12 respectively for Fe^{2+} and 10-12 for Zn^{2+}

and Ni^{2+} ions, the extent of removal of metal ion decreases. This decrease may be due to the formation of soluble hydroxyl complexes. But from pH 4-8, there is increase in removal for all three metal ions and with increasing pH, electrostatic repulsion decreases due to reduction of positive charge density on the sorption sites thus resulting in an enhancement of metal adsorption (Bhattacharya A K *et al.*, 2006). From the analysis of the treatment, the results showed a good reduction at pH of 8 for Fe^{2+} to reduced Fe^{2+} from 13.790 to 1.436 mg/l (89.58% removal), while Zn^{2+} and Ni^{2+} show a good reduction at pH 10 to give good reduction of Zn^{2+} from 1.650 to 0.127 mg/l (92.30% removal) and Ni^{2+} was reduced from 2.000 to 0.115 mg/l (94.22% removal). Fe^{2+} which should be precipitated at pH 8 in accordance to literature (Xinchao., 2005). The reason for precipitation across the pH range may be due to progressive oxidation of Fe^{2+} to Fe^{3+} by oxygen in the air and its precipitation in form of $\text{Fe}(\text{OH})_3$. This tremendous increase in percent reduction of metal ions with increase in pH up to 8 for Fe^{2+} and pH 10 for Zn^{2+} and Ni^{2+} is due to the fact that decomposition of H_2O_2 is favoured by increasing pH especially at pH 6–8 for Fe^{2+} and 8-10 for Zn^{2+} and Ni^{2+} (Pignatello J., Oliveros E., Mackay A., 2006). Removal of metal ions at higher pH values could be attributed to the formation of their hydroxide which results in precipitation, this is consistent with observation of Xiao and Ju-Chang., 2009).

5. Conclusion and Recommendation

In conclusion this study has revealed that there are much of heavy metals present in wastewater released by the pharmaceutical industry studied and likewise the study shows that heavy metals such as zinc (Zn) and nickel (Ni) released by the industry examined have high concentration of 1.650 mg/l and 2.000 mg/l respectively which are higher than 1 mg/l of effluent standard stipulated by Federal Environmental Protection Agency of Nigeria (FEPA) and World Health Organization (WHO), with the exception of iron (Fe) which has low concentration of 13.790 mg/l compared to 20 mg/l effluent standard stipulated by the Federal Environmental Protection Agency of Nigeria (FEPA).

The study clearly shows that combination of hydrogen peroxide and activated bentonite clay respectively can be used effectively as adsorbent for removal of Fe^{2+} , Zn^{2+} and Ni^{2+} from pharmaceutical effluent. Removal of heavy metals in effluent was optimum at pH 10 for zinc (Zn) and nickel (Ni) and at pH 8 for iron (Fe), at temperature of 50°C, 0.75% hydrogen peroxide concentration dose and 100 minutes holding time, reducing the amounts from 13.790 to 1.436 mg/l of Fe, while 1.650 to 0.127 mg/l of Zn and 2.000 to 0.115 mg/l of Ni. The percentage differences in concentration for the heavy metals removal in industrial wastewater are as follows: Fe (89.58%), Zn (92.30%) and Ni (94.22%). The removal of heavy metals; Fe, Zn and Ni using combination of H_2O_2 and activated bentonite clay was found to be effective and was enhanced based on pH effect causing increase in the breaking down of H_2O_2 molecule to H_2O and O_2 . The results obtained show that combination of hydrogen peroxide and

activated bentonite clay can be used effectively in the removal of heavy metal ions from industrial wastewaters.

It is therefore recommended that from the results obtained in this study and field observation during sampling, the following recommendation are been offered;

- Industries which have some heavy metals at levels above the FEPA and WHO permissible limits in their effluents should employ more rigorous methods for the treatment of their effluents before discharge to the environment.
- Heavy metals are not the only pollutants in industrial effluents. Constant environmental monitoring should be encouraged checking the levels of other pollutants present in these effluent to ensure compliance with acceptable standards.
- Government should enforce the sound environmental disposal of industrial effluents since most of these industries carelessly dispose this wastewater into open land and waterways.
- Manufacturing industries should employ the services of quality control personnel to check the pollution load of their effluents before disposal to the environment.
- The assessment of trace organic and microbial pollutants in this effluent may be an area of further research in this study.

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