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Remediation of Pharmaceutical Wastewater Using Azadirachta Indica Bark

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Abstract
The large development of pharmaceutical industries led to enormous quantity of freshwater being utilized, which generates large amounts of wastewater. This wastewater contains pollutants of which heavy metals are part of. Heavy metals can be treated by different methods, but adsorption is considered to be an effective method. This study dealt with heavy metals such as Chromium, Copper, Zinc, Lead and Cadmium. Raw pharmaceutical wastewater sample needed for this research collected from Sam'Ace pharmaceutical company Akoda Estate, Ede, in south Western Nigeria was characterized for physicochemical and heavy metals. Azadirachta Indica Bark also known as Neem Tree locally called DONGOYARO used as adsorbent for this study was acquired from Ladoke Akintola University of Technology Teaching and Research Farm, Ogbomosho, Nigeria. The characterized raw wastewater sample for physicochemicals; Turbidity (T), Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), pH, Total Dissolved Oxygen (TDS), Dissolved Oxygen were: 4.29mg/L, 137.3mg/L, 3.31mg/L, 4.14mg/L, 0.49mg/L, 0.65mg/L, respectively. Results of 1.0 gram of ZnO Nanoparticle (NP) gave a percentage decrease of 62%, 18%, 54%, 50%, and 28% for BOD, COD, DO, T, TDS and 5%, 6%, 9.1%, 7.4%, 16.7% for Chromium, Cadmium, Lead, Zinc, and Copper. Result of 2.5 gram of ZnO NPs gave a percentage decrease of 65.6%, 27%, 58.5%, 51.2%, and 59.2% for BOD, COD, DO, T, TDS and 8.6%, 16.5%, 27.3%, 23.8%, for Chromium, Cadmium, Lead, and Copper. Result of 5.0 gram of ZnO NPs gave a percentage decrease of 66.8%, 41.6%, 61.5%, 52.4%, and 75.5% for BOD, COD, DO, T, and TDS.

Keywords: *Pharmaceutical wastewater, Azadirachta Indica Bark, Heavy metals, Chemical oxygen demand, Biochemical oxygen demand, pH, Total dissolved oxygen, Dissolved oxygen*

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1. Introduction

The indiscriminate discharge of industrial wastewater into water bodies due to increasing human activities is a grievous environmental problem. The depletion of living organisms at a sudden rate in the ecological environment is caused by these activities (Shirafkan et al., 2016). The pollutants (especially toxic metals) caused by the presence of industrial wastewater in the ecological environment usually result in the continuous presence of pollutants in the food chain and negative effects on living creatures in the environment (Kariuki et al., 2017). Some toxic metals are used in the production of batteries, solders, bearings, ammunition, cement, paper, rubber, etc.; its ingestion by human beings is injurious to human health (Ojoawo et al., 2016). In the last decades, toxic metal pollution has become a serious environmental issue due to the serious harm they cause (Smily and Sumithra, 2017). Toxic metal pollution comes from the wastewater of many industries such as metal plating, mining operations, radiator manufacturing, smelting, alloy and batteries industries, etc.

Many methods such as chemical precipitation, ion exchange, electro-deposition, liquid–liquid extraction, membrane separation, reverse osmosis and coagulation, etc. have been used by many researchers for the removal of toxic metals from wastewater. High concentrations of toxic metals, huge cost and the production of large quantities of sludge among others are their disadvantages

(Abdelrahim et al 2002). The present need to remediate toxic metals from wastewater and the environment brought about a suitable and acceptable method called bio-sorption. It has been generally accepted due to its efficiency in removing toxic metals from wastewater at low cost, using simplified operation and low amounts of chemicals, and allowing the regeneration of adsorbents through desorption. In biosorption, the metal absorption is carried out by biological media, which bind the metals through adsorption, ion exchange and completion using presence of some definite functional groups e.g. alcohols, phenols, etc. (Manjunatha and Vagish 2016).

The use of agricultural bioresources (e.g. Azadirachta indica (Neem) leaves and seeds) in the remediation of toxic metals from synthetic wastewaters has been reported by many researchers – Alalwan and Alminshid 2020; Suleiman 2015; Shaik et al 2015; Smily and Sumithra 2017, among others. Azadirachta indica (the neem tree) belongs to the Malecite family, is native to Southeast Asia regions and can be found in many parts of the world. Its products have been extensively used and shown to be successful for solving various problems in agriculture, environmental contamination, health and population control (Majithya, et al., 2013).

2. Materials and methods

2.1 Collection of pharmaceutical wastewater

The pharmaceutical wastewater sample for the study shown in Fig. 1 was collected at *Sam` ace pharmaceutical company Km 14, gbongan road, Akoda ede, Ede, Osun state, Nigeria* in a sterilized 50-litre and transferred to the Environmental Engineering Laboratory, Department of Civil Engineering, Adeleke University, Ede, Osun State, Nigeria for analysis.

Fig. 1: Pharmaceutical wastewater sample

2.2 Analyses of raw pharmaceutical wastewater

The physicochemical analyses were conducted on raw wastewater sample. Physical parameters analyzed were pH, and turbidity. Chemical analyses conducted were dissolved oxygen, chemical oxygen demand, biochemical oxygen demand, total dissolved solids. Heavy metals analyzed are copper, zinc, chromium, cadmium, lead.

2.3 Determination of pH

The pH was determined by directly dipping the electrode of the table top pH meter (PH-550) in a plastic container containing the sample. Calibration was carried out using buffer solutions of pH 4.0, pH 7.0 and pH 10.

2.4 Determination of dissolved oxygen procedure

Dissolved oxygen (DO) was determined in-situ, using a battery operated JENWAY dissolved oxygen meter. The probe of the meter was dipped directly and gently into the water body without disturbing the water body, and the dissolved oxygen content (mg/L) was read and recorded immediately on the field.

2.5 Determination of biochemical oxygen demand

Biochemical oxygen demand (BOD) was determined by measuring the dissolved oxygen content of the sample on a given day, then incubating the sample, and repeating the DO determination after incubation for five days. The difference is a measure of the BOD.

2.6 Preparation of reagent

Ferric chloride: 0.125g of ferric chloride, $FeCl_3.6H_2O$ was dissolved in 1L water. Calcium chloride solution: 27.5g of calcium chloride, $CaCl_2$, was dissolved in 1L distilled water. Magnesium sulphate solution: 25g magnesium sulphate, $MgSO_4.7H_2O$ was dissolved in 1L distilled water. Phosphate Buffer Stock Solution: 42.5g potassium dihydrogen phosphate, KH_2PO_4, was dissolved in 700mL distilled water and 8.8g NaOH was added to this and mixed. This gave a pH of 7.2. Then, 2.0g ammonium sulphate was added and diluted to 1L.

2.7 Preparation of dilution water

Exactly 1mL of each reagent stock solution was added to 1000mL of freshly distilled water. The water was brought to incubation temperature at 20±1. Aerated dilution water was then prepared by saturating this with oxygen, by bubbling air through it using a vacuum pump. Procedure: 200mL of saturated dilution water was added to 300mL BOD bottle. A measured volume of water sample was then added to this, and mixed with it. Initial dissolved oxygen content (DO_1) was then measured; using a dissolved oxygen meter. The sample in the BOD bottle was then incubated for 5 days at a temperature of 20^0 and in the dark. After five days of incubation, the dissolved oxygen content (DO_5) was again determined.

2.8 Determination of chemical oxygen demand

The chemically oxidizable organic matter content of a given sample is oxidized with known excess amount of acidified potassium dichromate. Unreacted dichromate is then determined by redox titration with ferrous sulphate.

2.9 Determination of turbidity

Turbidity determination was carried out by UV-visible JENWAY Model7305 spectrophotometer.

2.10 Determination of total dissolved solids

A portable TDS meter was dipped into a plastic container containing the sample, and the TDS value read immediately. Replicate determinations were made to estimate precision. The TDS meter (HANNA) was calibrated with 0.02M KCl and 0.20M KCl.

2.11 Determination of minerals (heavy metals)

Mineral contents of samples were determined by atomic absorption spectrophotometer (AAS) according to the methods of AOAC (2003) at Redeemers University Ede, Osun state. Determination of Zinc (Zn), Chromium (Cr), Cadmium (Cd), Copper (Cu), and Lead (Pb), by Shimadzu Atomic Absorption Spectrophotometer model AA-6800,

2.12 Adsorbent material and preparation

The *Azadirachta indica* bark also known as Neem Tree and locally called DONGOYARO by Yoruba tribe for this study was acquired locally from Ladoke Akintola University of Technology (LAUTECH) Teaching and Research Farm, Ogbomosho, Nigeria. It was cut into pieces, thoroughly washed with distilled water to remove all possible impurities and contaminants, sun dried for a month and then grind into powder with Hammer mill the adsorbent will be prepared using ZnO (zinc oxide) as activating agents.

2.13 Preparation of synthesized zinc oxide Nano particles (ZnO NPs)

In synthesizing the nano-particles, *Azadirachta Indica* Bark powder was soaked for 24 hours and was then sieved and filtered, 150mL of distilled water was poured in a 250mL conical flask and 3g of zinc Acetate Dyhydrate was dissolved in the 150mL of distilled water and was stirred, measurement of 5 ml of filtered *Azadirachta Indica* Bark shown in Fig. 2 was added to the conical flask of zinc Acetate Dyhydrate and was stir for 30mins. The mixture was oven-dried until it was evaporated. Remove the residue (green synthesized nano-particles) and put in a sample test tube revealed in Fig. 3.

Fig. 2: 5ml of filtered *Azadirachta Indica* Bark

Fig**. 3:** Treated wastewater in test tube

3. Results and discussion

3.1 Characteristics of pharmaceutical wastewater

As indicated in Table 1, AAS detected the initial amounts of Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Cr^{3+} and in the pharmaceutical effluent sample. It showed that all initial heavy metal concentrations from pharmaceutical wastewater were higher than WHO (2011) and FEPA limits and concentrations from other areas, implying that mining wastewater may pollute soil, water bodies, and the ecosystem as a whole. Each heavy metal's concentration is displayed in milligram per litre (mg/L). The respective values were in decreasing order were: zinc (1.24 mg/L) > chromium (1.15 mg/L) > cadmium (0.85 ppm) > copper (0.42 mg/L) > lead (0.11 mg/L). And each physicochemical is displayed in milligram per litre. The respective values were in increasing order were: Total dissolved solid (0.49 mg/L) < Dissolved Oxygen (0.65 mg/L) < Biological oxygen demand (3.31 mg/L) < pH (4.14) < Turbidity (4.29 mg/L) < Chemical oxygen demand (137.3 mg/L). The FEPA limit for BOD is 50 mg/L for any surface water discharge; therefore, if the raw wastewater from the present study is released into any surface water without pre-treatment, it will cause untold harm to the users of the water and the aquatic life in the water. This assertion is supported by the publication of FEPA.

Furthermore, pharmaceutical wastewater typically has a high chemical oxygen demand (COD) from all the organic components (sugar, soluble, starch) (Changotra et al., 2019). This is further buttressed by the analysis of the present study as the result of the COD was found analytically to be 137.3 mg/L of COD in Table 1 as well. When compared with the publication of FEPA, the result of the study falls considerably above the permissible limit which is 80 mg/L, the raw wastewater sample used in this study may not be released into any surface water without treatment in order not to put the integrity and safety of the environment at risk of pollution. The concentration of total dissolved solids is 0.49. The concentration of total dissolved solids is far lower than the recommended limit of 2000 mg/L by FEPA. The values of the heavy metals (Table 1) are 0.11 mg/L, 0.42 mg/L, 1.24 mg/L, 0.85 mg/L 1.15 mg/L and for Pb, Cu, Zn, Cd, and Cr, respectively. The analyzed value of Cu is within the permissible limit prescribe by FEPA (1992) for wastewater to be released into the environment. However, the analyzed value of the Lead, cadmium and Chromium is above the permissible limit prescribed by FEPA (1992) meaning that releasing the wastewater sample untreated will be unwholesome to the environment. The findings of Menkiti et al (2015) concluded that when wastewaters with high values of heavy metals are released untreated into the environment, humans and animals that use such waters are at risk of cancers and congenital diseases.

Table 1: Characteristics of pharmaceutical wastewater

Physicochemical properties (mg/L)	Value
Turbidity (mg/L)	4.29
Dissolved oxygen (mg/L)	0.65
Chemical oxygen demand (COD) (mg/L)	137.3
Biological oxygen demand (BOD) (mg/L)	3.31
pH (mg/L)	4.14
Total dissolved solid (TDS) (mg/L)	0.49

Table 2: Characteristics of treated pharmaceutical wastewater

Heavy metals (mg/L)	Value
Lead (Pb)	0.11
Copper (Cu)	0.42
Zinc (Zn)	1.24
Cadmium (Cd)	0.85
Chromium (Cr)	1.15

3.2 Treatment of raw pharmaceutical wastewater

The raw wastewater was subjected to treatment using three concentrations of the treatment materials; 1.0g ZnO NPs to 100mL wastewater, 2.5g ZnO NPs to 100mL wastewater, 5.0g ZnO NPs to 100mL wastewater as shown in Table 2. When treated with 1.0g ZnO NPs the physicochemical parameters such as BOD, COD, DO, NTU, TDS reduced by 62%, 18%, 54%, 50%, 28% respectively and the heavy metals Chromium, Cadmium, Lead, Zinc, Copper were also reduced by 5%, 6%, 9.1%, 7.4%, 16.7% respectively. These results also shows that the addition of 1.0g ZnO NPs has significant remediation effects on the physicochemical parameters and heavy metals of pharmaceutical wastewater.

When treated with 2.5g ZnO NPs the physicochemical parameters further reduced by BOD-65.6%, COD-27%, DO-58.5%, NTU-51.2%, TDS-59.2% and for heavy metals are reduced by Cr- 8.6%, Cd-16.5%, Pb-27.3%, Cu-23.8% respectively and for Zinc it remains constant and was not reduced from 7.4%. These results also shows that the addition of 2.5g ZnO NPs has significant remediation effects on the physicochemical and heavy metals of pharmaceutical wastewater except Zinc.

When treated with 5.0g ZnO NPs, the amount of the physicochemical parameters decreased further (BOD-66.8%, COD-41.6%, DO-61.5%, NTU-52.4%, TDS-75.5%) indicating that the synthesized Zinc Oxide nano-particles had a great effect on the pharmaceutical effluent. The results obtained showed that the concentration of Cr, Cd, Pb, Zn and Cu reduced by 14.8%, 21.2%, 63.6%, 8.1%, 30.9%) respectively. These results showed that the addition of 5.0g ZnO NPs is the recommended optimal performance value because it has significance remediation effects on the physicochemical parameters and heavy metals of the pharmaceutical wastewater as analysed.

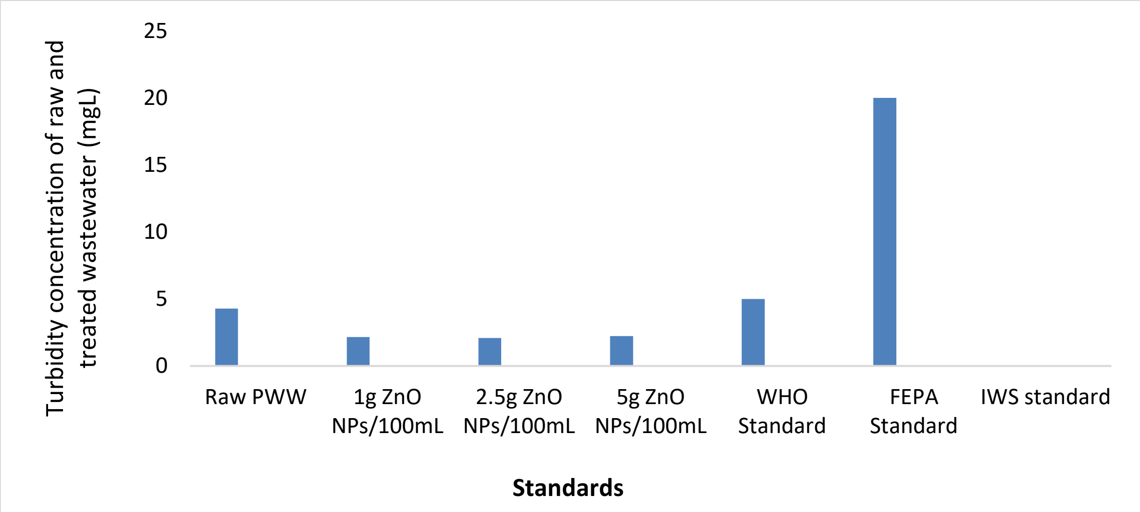

Fig. 4: Turbidity concentration of raw and treated wastewater compared with standards

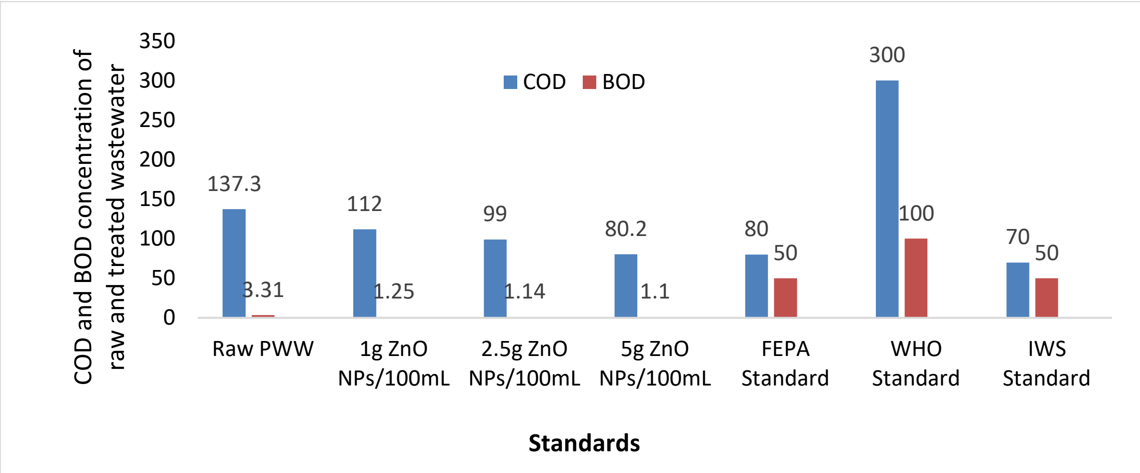

Fig. 5: COD and BOD concentrations of raw and treated wastewater compared with standards

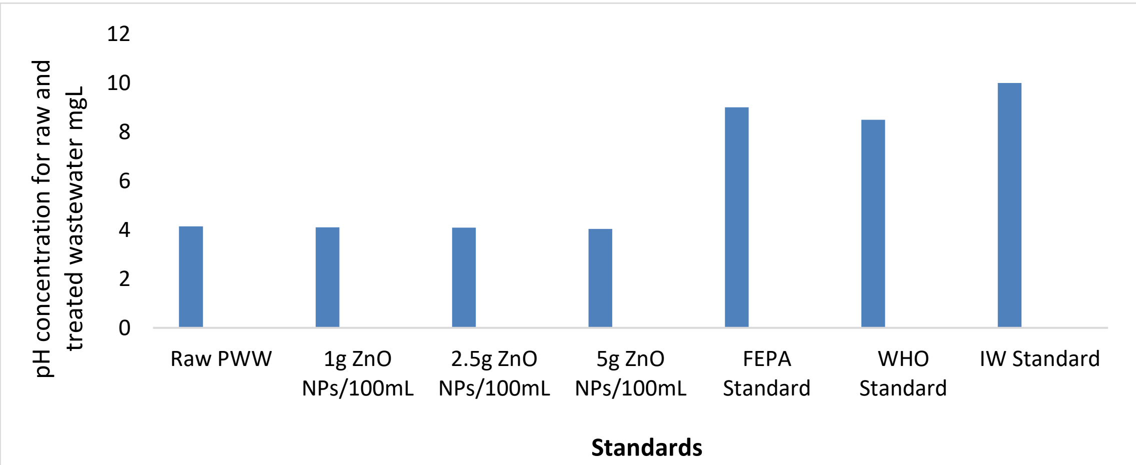

Fig. 6: pH concentration of raw and treated wastewater compared with standards

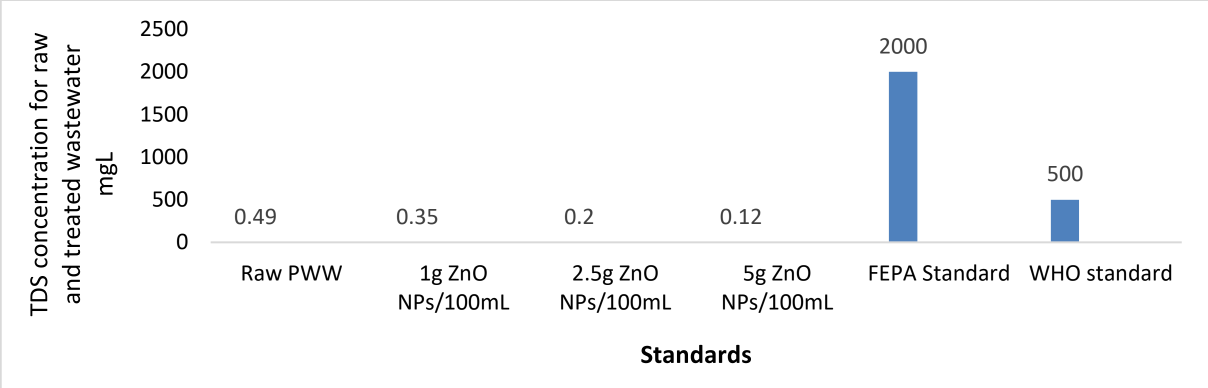

Fig. 7: Total dissolved solid for raw and treated wastewater compared with standards

4. Conclusion

The characteristics of the raw pharmaceutical wastewater obtained from Sam'Ace pharmaceutical Company, Akode, Ede showed that the raw pharmaceutical water was polluted and the analysis carried out equally revealed that some of the physico-chemical and heavy metals parameters were above FEPA, WHO and industrial waste standards. Treatment of the wastewater using the green synthesized nano-particles showed a considerable reduction in content of physico-chemical parameters and the results are within FEPA, WHO and industrial waste standards recommended value for treated effluents. Treating the raw wastewater with 5.0g ZnO NPs is the most effective among the varying grams used, the percentage of the heavy metals Cr, Cd, Pb, Zn and Cu reduced by 14.8%, 21.2%, 63.6%, 8.1%, 30.9%) respectively. Also, BOD_5, COD, DO, NTU, TDS reduced by 66.8%, 41.6%, 61.5%, 52.4%, and 75.5% respectively.

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