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Photocatalytic Removal of Toxic Metals from Tannery Wastewater using Green Synthesized Zinc Oxide Nanoparticles

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ABSTRACT

Water is an important natural resource and is vital to all living organisms. However, increased industrialization and urbanization have led to water pollution. This research aimed at removing some toxic metals from tannery wastewater using already green synthesized zinc oxide nanoparticles (ZnO-NPs). The treatment method used was photocatalytic degradation. The concentrations of Cr, Cu, and Pb in the wastewater were found to be above the standard recommended by WHO and the National Environmental Standards Regulatory and Enforcement Agency (NESREA) while those of Ni, Mn, and Co were within the acceptable limit. The photocatalytic degradation using the ZnO-NPs was effective in the treatment of the metals: Cr, Co, Cu, Mn, Ni, and Pb as their concentration in the treated tannery wastewater were significantly lower than that in the untreated wastewater except for Mn. Based on the results, photocatalytic degradation using green synthesized ZnO-NPs has proven to be a viable method for the degradation of tannery wastewater.

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1. INTRODUCTION

Water is one of the most important natural resources in the world, which is vital for the survival of all living organisms. However, due to increased industrialization and urbanization, the consumption of water is increasing rapidly and the water scarcity problem has become an important constraint for economic development because several pollutants such as inorganic ions, organic pollutants, organometallic compounds, radioactive isotopes, gaseous pollutants have polluted the water environment (Briffa *et al*., 2020). Plants through different pathways take some of these contaminants up and they accumulate in the food chain as crops can even absorb and accumulate metals in their system (Okon *et al*., 2023). hence, compromising the safety of the food consumed by both humans and animals.

In the meantime, water contamination, especially heavy metals pollution inside water, has become a global environmental issue. Heavy metals could be released into water mainly through mining, electroplating, metallurgy, chemical plants, agriculture, and household wastewater among others. Intake of some toxic heavy metals such as Pb, Zn, Cu, Hg, and As by aquatic fauna can cause detrimental health problems in other animals and ultimately humans *via* the food chain. Heavy metals can be teratogenic, and carcinogenic and can cause oxidative stress, organ damage, nervous system impairments, and reduced growth and development (Cheraghi *et al.,* 2009). Leather is one of the fast-moving commodities, that is utilized in products like footwear, bags, and wallets among others, and the leather industry itself is one of the key players in the economy of nations (Oruko *et al.,* 2020). Despite its economic potential, the leather industry poses a serious environmental threat due to the generation of enormous wastewater and solid wastes and is also considered to be a major point source of environmental pollution and one of the major headaches facing legislators, because it produces large amounts of wastewater that contains different pollutants which create a negative image of leather tanneries in the society (Salem *et al.,* 2019). About 1 kg of animal skin processing consumes 35 to 40 L of high-quality water (Fouda *et al.,* 2021). Consequently, there is a great need for the removal of these toxic metals from the water bodies and this has drawn the attention of the scientific community.

In the literature, numerous strategies have been used for wastewater treatment, such as solvent extraction, sedimentation, gravity separation, microfiltration, ultrafiltration, precipitation, coagulation, distillation, oxidation, adsorption, electro-dialysis, electrolysis, flotation, ion exchange ultrafiltration, evaporation, and reverse osmosis (Naseem & Durrani, 2021). These methods require high energy and the usage of hazardous chemicals and might result in the production of several toxic substances (Kalsoom & Batool, 2020). Presently, most scientists have come to believe that nanomaterials are one of the mainstays of emerging science and technology due to larger specific areas, lower modification of temperature, tunable pore size, the shorter distance of inter-particle diffusion, the large number of associated adsorption sites, and differing surface chemistry compared to other materials, nanoparticles are considered to be marvelous remarkable absorbents and catalysts that can be used in environmental remediation (Gong *et al.,* 2018). Nano- bioremediation is the use of green synthesized nanoparticles (NPs) to clean- up environmental pollutants (Ye *et al.,* 2019) and is considered a safe approach to environmental pollution control. Nanoparticles have recently emerged as promising agents for photocatalytic applications. The unique physicochemical properties of nanoparticles like higher surface area-to-volume ratio, size confinement, a significant increase in the band gap energy, and possession of higher redox potential in the system have been extensively examined for wastewater treatment (Abbasi *et al.,* 2018).

Until today, many photocatalysts (including ZnO and TiO_2) have been studied for the degradation of a wide range of dyes, pharmaceuticals, and organic/inorganic compounds like heavy metals. These two catalysts are the most preferable options because they are cheaper and have higher catalytic activity in degrading industrial pollutants compared to other semiconductors (Jafar *et al.,* 2019) but due to certain drawbacks attributed to the use of TiO_2, the focus of the scientific community have been shifted towards the use of ZnO (Khan & Pathak, 2020).

One of the major setbacks of TiO_2 is that it is a UV-light active photocatalyst and absorbs a very small portion of the solar spectrum (4–5%) unlike ZnO which absorbs more light quanta and acts as a semiconductor due to its band gap and electronic structure characterized by filled valence band and conduction band (Raizada *et al.,* 2019). ZnO is regarded as a good photocatalyst due to its high chemical stability and excellent photocatalytic activity when removing water pollutants. ZnO is a promising material for conducting photocatalytic activity because of its physical and chemical characteristics such as its high electrochemical stability, super oxidative capability, and low toxicity. ZnO is therefore the first and most commonly used material for heterogeneous photocatalysis among other metal oxides (Naseem & Durrani, 2021). This research therefore aimed at removing some toxic metals from tannery wastewater using already green synthesized zinc oxide nanoparticles

2. METHODS

2.1. Sample Collection and Pre-treatment

The tannery wastewater used for the study was obtained from the Tan Yard of the Nigerian Institute of Leather and Science Technology (NILEST), Zaria, Kaduna state, Nigeria. Samples of the tannery wastewater for analysis were collected in a 120 mL plastic container, which was initially washed with detergent, rinsed with distilled water, and finally rinsed with 20% HNO_3 and allowed to dry before sampling (Todorovi *et al.,* 2001). The wastewater was filtered to remove suspended solids.

2.2. Photocatalysis

100 ml of the wastewater was mixed with 80 mg amount of green synthesized zinc oxide nanoparticles (ZnO-NPs) made from Corchorus olitorius leaf extract as a reducing agent and zinc acetate dihydrate, $Zn(CH_3COO)_2.2H_2O$ as a precursor. The mixture was poured into a 200ml beaker, and then placed on a halogen lamp and magnetically stirred for 30 minutes in the dark to establish adsorption-desorption equilibrium of the components of the tannery on the ZnO-NPs photocatalyst. Thereafter, the mixture was exposed to visible light irradiation provided by a 300W halogen lamp under continuous stirring at room temperature (25±2°C) (Boruah *et al.,* 2020). The total metal content of the raw and treated samples of the tannery wastewater was determined using a Microwave Plasma Atomic Emission Spectrophotometer (MPAES, model 4200, USA) in the Multi-User Science Research Laboratory of Chemistry Department, Ahmadu Bello University, Zaria. Previous works on the adsorption and photocatalytic removal of toxic metals using various adsorbents and photocatalysts concluded that the removal efficiency is highest in an acidic medium with a pH of 2.5 – 4.0 (Boruah *et al.,* 2020). Therefore, the experiments were performed at a pH of 3.0.

2.3. Digestion of Wastewater Samples

The water samples were mixed thoroughly by shaking. A 50 ml filtered aliquot of wastewater sample was pipetted into a digestion flask. The wastewater was digestion in 3 ml concentrated HNO_3 and 3 ml H_2O_2 below 80°C for 1 h until a clear solution was observed. The clear solution was diluted to 100 ml in a volumetric flask with distilled water. Blank digestion was also carried out in the same way (Birtukan & Gebregziabher, 2014). The blank solution contained all reagents except wastewater. All samples were digested in triplicates (Okon *et al.*, 2022). The digests were analyzed for the heavy metals by using the Microwave Plasma Atomic Emission Spectrophotometer (MPAES, model 4200, USA). The concentration of each metal was calculated using the formula below (Aga & Brhane, 2014).

$$\text{Final concentration } \left(\frac{\text{mg}}{\text{L}}\right) = \frac{\text{CM} \times \text{DF} \times \text{NV}}{\text{SV}} \times 100 \quad (1)$$

Where *CM* is the Concentration of metal, *DF* is the Dilution factor, *NV* is the Nominal volume, and *SV* is the Sample volume (mL).

2.4. Statistical Analysis

The data obtained was subjected to the statistical test of significance using the Paired Samples Test to assess significant variation in concentrations of toxic metals in the untreated and treated tannery wastewater at a 95% confidence level ($p < 0.05$) using The Statistical Package for Social Sciences (SPSS) software 20.00 for windows.

3. RESULTS AND DISCUSSION

The mean value of total Cr in the untreated tannery wastewater was 1.250±0.01 mg/L (See **Figure 1**), this is higher than the NESREA permissible limit of 0.5 mg/L while that of treated wastewater was 0.0725±0.01 mg/L which is below the NESREA standard limit. At high concentrations, chromium is toxic, mutagenic, carcinogenic, and teratogenic. Cr has drawn greater attention in the present context of global ecology as its toxicity may damage human organs including the kidneys and liver as well as cause dermatitis and gastrointestinal ulcers (Mia *et al.,* 2020).

One of the major pollutants present in city wastewater used for irrigation in some developing countries is cobalt (Khan *et al.,* 2020), even though it is not an essential element for plants (Ugulu, 2015a). Since excessive amounts of cobalt in agricultural areas have toxic effects on cultivated plants, it is undesirable to be found in agricultural soils, especially at amounts higher than the permissible level (Khan *et al.,* 2018).

For this reason, the amount of cobalt in the soil solution is extremely significant for plants. The root apices of plants are impassable with heavy metals due to their immature cells and low-density cell walls. The root cells absorb the toxic metals from the contaminated soil and then these elements are transferred to the upper parts of the plants (Tung & Temple, 1996). The value of Co in the untreated tannery wastewater was found to be 0.203±0.00 mg/L (See **Figure 1**), this is less than the WHO/NESREA value of 0.5 mg/L while in the treated wastewater sample, the value was beyond the detection limit.

The amount of Cu in the untreated tannery wastewater was observed to be 0.190±0.00 mg/L and that of the treated wastewater was 0.155±0.00 mg/L. Though both concentrations are above the WHO standard limit of 0.1 mg/L, the concentration in the untreated wastewater (0.190±0.00 mg/L) was higher than that of treated wastewater (0.155±0.00 mg/L). The value observed was higher than the 0.022 mg/L obtained by other researchers (Deepali, 2010). Some researchers (Bernard and Ogunleye, 2015) reported values of Cu at a concentration range of 0.82 - 1.51 mg/L, similarly, high concentrations were earlier reported in Kano State (Dan'Azumi & Bichi, 2010). Cu is an integral part of numerous enzymes, normal copper homeostasis is essential for human growth and development, as well as for disease control in livestock and poultry, a cofactor in enzymes including ferroxidase (ceruloplasmin), cytochrome – c –oxidase, superoxide dismutase, and others. It plays a role in iron metabolism, melanin synthesis, and central nervous system function, but at high concentrations, it affects the liver and causes kidney damage and gastrointestinal distress (Ferreira & Gahi, 2017).

The value of lead (See **Figure 1**) in the untreated tannery wastewater was found to be 1.862±0.0026 mg/L, this is above the WHO/NESREA standard of 0.1 mg/L, the value in the treated tannery wastewater was 1.463±0.0125, which is lower than that of the untreated but is also higher than the WHO/NESREA standard limit. Lead affects the central nervous system, particularly in children, and also damages the liver, kidneys and the immune system, at higher concentrations, lead may result in metallic poisoning which can cause cancer in humans (Shaibu & Audu, 2019).

Nickel concentration (See **Figure 1**) in the untreated tannery wastewater was found to be 0.539±0.0005, this is below the WHO/NESREA Standard of 1.0 mg/L while that of the treated was 0.276±0.0006 which was also below the WHO/NESREA standard limit. However, the concentration in the untreated wastewater was higher than that of the treated wastewater. values reported in literatures were 0.05 mg/L, 0.68mg/L and 0.85mg/L (Bhatnagar *et al.,* 2013; Amenial, 2015), respectively. The presence of nickel in tannery wastewater may be attributed to chemicals used in the tanning and post-tanning processing of leather. At high concentrations, nickel may cause damage to DNA and cell structures.

Values of Mn in the untreated and treated tannery wastewater were 0.023±0.00 and 0.0082±0.00, all were below the WHO/NESREA standard limit. Though the concentration in both the treated wastewater sample and untreated wastewater sample was lower than the WHO/NESREA limit of 0.2 mg/L, the concentration in the treated was lower than that observed in the untreated. Some researchers Yusuff and Sonibare (2004) reported a higher Mn value of 0.988 mg/L in tannery wastewater obtained from Lagos.

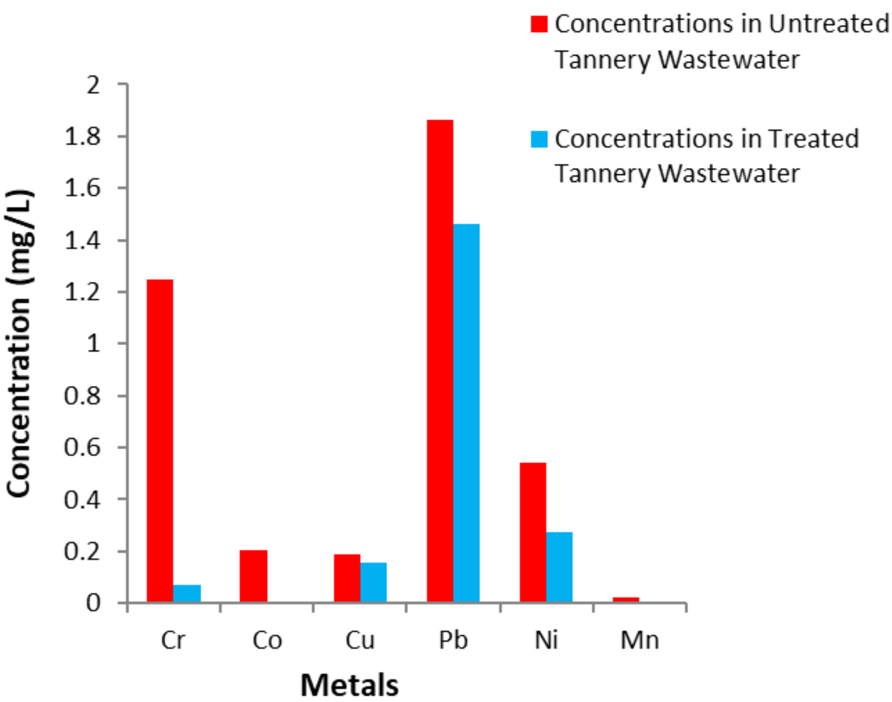

Figure 1. Concentration of metals in untreated and treated tannery waste.

Results of the Paired Samples Test analysis (See **Table 1**) indicate that the variations in the concentration of heavy metals between the untreated and treated wastewater samples were statistically significant ($p < 0.05$) for all the heavy metals tested except for Mn. This is an indication that the treatment process is effective.

Table 1. Paired Samples Test for the Metal content of the untreated and treated wastewater sample

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Eror Mean	95% Confidences interval of the Difference				
Pair1	Cr_u/Cr_t	3.12917	0.21000	0.12125	2.60749	3.65085	25.808	2	0.001
Pair2	Co_u/Co_t	0.20100	0.02007	0.01159	0.15113	0.25087	17.342	2	0.003
Pair3	Cu_u/Cu_t	0.03167	0.00289	0.00167	0.02450	0.03884	19.000	2	0.003
Pair4	Pb_u/ Pb_t	0.42633	0.06450	0.03724	0.26610	0.58656	11.448	2	0.008
Pair5	$Ni_u - Ni_t$	0.27767	0.01365	0.00788	0.24376	0.31158	35.232	2	0.001
Pair6	$Menu/Mn_t$	-0.05900	0.05237	0.03024	-0.18910	0.07110	-1.951	2	0.190
Pair2	Co_u/Co_t	0.20100	0.02007	0.01159	0.15113	0.25087	17.342	2	0.003

4. CONCLUSION

Photocatalytic degradation using green synthesized zinc oxide nanoparticles (ZnO-NPs) for the treatment of metals: Cr, Co, Cu, Mn, Ni, and Pb was effective as their concentration in the treated tannery wastewater was significantly lower than that in the untreated tannery wastewater except for Mn. Hence, Photocatalytic degradation of tannery wastewater using green synthesized ZnO-NPs is a viable method considering the metals studied.

5. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. Authors confirmed that the paper was free of plagiarism.

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