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Evaluation of the Efficiency of a Bio-Derived MgO Nano Powder Adsorbent in the Reduction Of COD, ORP, TDS, pH and EC of Tannery Wastewater

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ABSTRACT
The tannery is responsible for the introduction of tannery wastewater into the environment and this wastewater contains high concentration of Chemical oxygen demand (COD) and other physiochemical parameters. the study of the performance of COD and physiochemical parameter degradation via adsorption was taken using Bio-derived MgO nano powder (MgO-p), synthesis using extract of locust beans and Mg (NO3)2 at 500oC following a green approach. The reduction efficiency of the MgO-p was evaluated in the presence of raw tannery wastewater by application of treatment time, adsorbent dosage, pH and concentration as parametric factors, and physicochemical properties such as Total dissolved solid (TDS), Electrical conductivity (EC), Oxidation-reduction potential (ORP) and pH. Result obtained were compared to environmental regulatory limits (WHO and NESERA). Concentration reported removal efficiency of 42.8% to 78.5% for COD, adsorbent dosage reported removal efficiency of 5.71 to 100, COD; contact times reported removal efficiency of 57.1 to 71.42% and pH reported removal efficiency of 5.7 to 50%. This study reveals that MgO powder is better applied as COD removal agent over other physicochemical parameters for tannery effluent treatment.

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INTRODUCTION

In recent times, the field of adsorption studies has witnessed additions of a variety of efficient, eco-friendly and cost-effective nano-materials, that find application in the decontamination of industrial and domestic liquid wastes (Theron *et al*., 2018). Treatment of wastewater and drinking water can reduce contamination concerns (Ferroudj *et al*., 2013); however, existing traditional methods of treatment in practice are not efficient enough to completely remove emerging contaminants (Ferroudj *et al*., 2013), thus, the emphasis on a more efficient, cheaper and powerful green technology for the treatment of municipal and industrial wastewaters (Ferroudj *et al*., 2013). A variety of efficient, eco-friendly and cost-effective nano-materials with unique functionalities for potential decontamination of industrial effluents, surface water, groundwater and drinking water have been employed in wastewater treatment (Gupta *et al*., 2015; Theron *et al*., 2008). From documented evidence, nano-technology has a proven ability to remediate wastewaters (Zare *et al*., 2013; Sadegh *et al*., 2014), because structurally, they are components with a dimensional size of at least below 100 nm (Amin *et al*., 2014). COD levels in wastewaters are serious environmental concerns and could present detrimental effects especially when their presence exceeds environmental standards (Ramasami *et al*., 2015)

Nanomaterials exist in a variety of forms, including nano-wires, nano-tubes, films, particles, quantum dots and colloids, all having excellent liquid treatment potential (Dutta and Maji, 2014). Nano-adsorbent can be produced using atoms of elements that are chemically active and having high adsorption capacity on the

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surface of the nano-material (Kyzas and Matis, 2015). Activated carbon, silica, clay materials, metal oxides and modified compounds in the form of composites are examples of nano-adsorbents employed for wastewater treatment (El-Saliby *et al*., 2018).

The use of metal oxide-based nanoparticles as adsorbents is gaining recognition in environmental sciences. Researches on MgO and CuO based nanoparticles for photocatalytic and biological activities have also been published. Oladipo *et al*., (2017), reported the synthesis of a bio-derived MgO non-powder and applied it in the reductive treatment of COD in tannery wastewater; with results showing a 93.5% and 96.9% removal. Because industrial activities vary, so also will the wastes they generate (both physical and chemical parameters), with pollution levels rising beyond prescribed levels. Untreated effluents when released into receiving water bodies (rivers, lakes, ponds, etc.), are a major contributor to water pollution (Rehman and Anjum, 2010). Spent Tan liquor from leather industries characteristically, in addition to metal contaminants contains high concentrations of organic particles and sediments, accounting for its high COD (Chemical Oxygen Demand) levels (Ramasami *et al*., 2015).

Tannery industry is reputed globally as a major industry, which contributes to water pollution, owing to the usage of mineral tanning agents. They discharge large volumes of effluents, because except one or two process in the tannery industry, all the processes are wet processes and generate huge quantities of liquid wastes. The effluents are far from the desired level for acceptance into two ways with a heavy load of pollutants like chromium, chlorides, sodium, dissolved solids, COD, Nitrogen and suspended solids. Tannery effluents containing large amount of wastes especially tannins are toxic to plants, animals and soil as well as water microorganisms. In plants they cause stunting growth, chlorosis and reduction in yield. However, a few microorganisms degrade tannins and utilize their carbon source.

METHODOLOGY

Collection and preparation of leave extract

Fresh leaves of locust beans was collected from Savana Garden in Samaru Zaria, Kaduna State. The leaves was washed thoroughly with tap water to remove sand and other solid particles and then rinsed severally with distilled water, chopped into tiny bits, air-dried for 12 days, grounded to powder using mortar and pestle. A-50 g of powdered leaves was weighed out and added to 400 mL of distilled water in a 1000 mL conical flask and stirred under heat at 80 °C for 30 minutes. The extract was mixed and centrifuged for 10 minutes and then filtered, the filtrate was kept in the refrigerator for use in the synthesis of MgO-NP (Saikia *et al.,* 2015).

Green synthesis of MgO nanopowders

An aliquot of 150 ml of the aqueous plant extract was mixed with 20 ml of $Mg(NO_3)_2.6H_2O$ in a 400 ml conical flask. The mixture was vigorously stirred for 20 min at ambient temperature, forming milky precipitates and was collected by centrifugation. The precipitates was washed with ethanol, rinsed with distilled water, and dried at 90 °C for 3 hrs. The dried precipitate powder was heated in an oven at 500 °C for 2 hrs to form MgO nanopowder. (Feka *et al.* 2021)

Collection of tannery effluent

Tannery effluent was collected by spot (grab) sampling method as detailed elsewhere (UNIDO, 2016). Collected wastewater was filtered and stored in a cooling set, at freezing temperature (below 4 °C) till use.

Effect of concentration

A weighing balance was used to weigh 50 mg of adsorbent and mixed with wastewater by varying the concentrations 2.5 ml, 5 ml, 10 ml and 20 ml. It was then agitated at 200 rpm for 60 min after agitating it was filtered using whatman filter paper COD and physicochemical properties were tested.

Effect of Agitation Time

A weighing balance was used to weigh 50 mg of adsorbent and mixed with 50ml of wastewater and agitated at 200 rpm varying time

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10, 20, 40 and 80 min after agitating for varying times it was filtered using whatman, COD and physiochemical properties were tested.

Effect of Adsorbent dosage

Adsorbent dosages (2, 4, 8 and 16 mg) were weighed separately into 4 conical flask, 50 ml wastewater was added to each flask, then placed on a shaker and agitated at 200 rpm for 60 min. it was filtered using whatman, COD and physiochemical properties were tested.

Effect of pH

The pH of the wastewater was varied at 2, 5, 8 and 14; after which 50 mg of adsorbent was added. The mixture was agitated at 200 rpm for 60 min. It was filtered using whatman filter paper, COD and physicochemical properties were tested.

Determination of Chemical Oxygen Demand (COD).

The COD of untreated and treated effluents was analyzed according to the standard methods of APHA (2018). A 10.0 ml of the sample was collected in a sample bottle, 1.0 ml of $HgSO_4$ was added, 10 ml of standard potassium dichromate $K_2Cr_2O_7$ solution was added and silver sulphate Ag_2SO_4 was slowly added and heated for 2 hrs. The mixture was allowed to cool at room temperature. 2 drops of feroin indicator was added and the mixture was then titrated against ferrous ammonium sulphate till reddish brown colour is obtained as the end point.

Determination of pH, Electrical Conductivity, Total Dissolved Solids and ORP

The pH of each sample was measured using a multimeter. The glass electrode of the pH electrode was dipped in 20 ml of waste water, and pH was measured. The electrical conductivity of all the samples was determined using "Electrical Conductivity Electrode". Total dissolved solid was determined with a TDS electrode. The probe was rinsed with distilled water followed by the sample to be tested. The rinsed probe was allowed to stabilize in the sample for 1 min after which the TDS value was read directly in mg/l. The test was performed in duplicates on all the samples and average values recorded (Fawell, and Nieuwenhuijsen, 2014).

RESULTS AND DISCUSSION

The result of adsorption studies and physiochemical properties of tannery wastewater using MgO Nano Powder from Locust beans extract, percentage yield and removal efficiency is presented below

Table 1: Physiochemical properties of untreated wastewater

TDS (ppm)	EC (S/m)	pH	ORP (mV)	COD (mg/l)
1590	1.0	4.35	179	14.00

Table 2: Effect of Concentration

Concentration	TDS (ppm)	EC (S/m)	pH	ORP (mV)	COD (mg/l)
2.5ml	20	0.03	3.92	189	7.00
5ml	310	0.44	1.67	304	3.00
10ml	5070	0.09	4.40	204	8.00
20ml	2840	4.09	4.01	194	8.00

Table 3: Percentage Removal Efficiency

Concentration	TDS (%)	EC (%)	pH (%)	ORP (%)	COD (%)
2.5ml	98.7	97	9.8	-0.55	50.00
5ml	80.5	56	61.6	-670	78.57
10ml	-218.8	91	-1.14	-15.08	42.86
20ml	-78.6	-309	5.97	-1.11	42.86

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Table 4: Effect of Agitation Time

Contact Time (Min)	TDS (ppm)	EC (S/m)	pH	ORP (mV)	COD (mg/l)
10	1649	16.47	3.68	202	6.00
20	1814	18.11	1.80	059	4.00
40	4950	6.86	3.68	197	4.00
80	1688	18.99	4.04	204	4.00

Table 5: Percentage Removal Efficiency

Contact Time (Min)	TDS (%)	EC (%)	pH (%)	ORP (%)	COD (%)
10	-3.71	-1547	58.6	-12.84	57.14
20	-14.08	-1711	15.4	67.03	71.42
40	-211.3	-586	13.40	-7918	71.42
80	-211.3	-586	7.12	-13.96	71.42

Table 6: Effect of Adsorbent Dosage

Adsorbent dosage	TDS (ppm)	EC (S/m)	pH	ORP (mV)	COD (mg/l)
2mg	1669	0.26	4.28	180	6.00
4mg	1812	0.16	1.76	299	6.00
8mg	1720	0.15	3.48	206	5.00
16mg	1711	0.10	4.46	181	7.00

Table 7: Percentage Removal Efficiency

Adsorbent dosage	TDS (%)	EC (%)	pH (%)	ORP (%)	COD (%)
2mg	-4.96	74	1.60	-0.55	57.14
4mg	-13.96	84	3.95	-6.70	57.14
8mg	-8.17	85	2.0	-15.08	64.2
16mg	-7.61	90	-2.52	-1.11	50.00

Table 8: Effect of pH

pH	TDS (ppm)	EC (S/m)	pH	ORP (mV)	COD (mg/l)
2	80	0.11	2.00	257	8.0
5	20	0.02	5.0	235	7.0
8	10	0.02	8.0	233	7.0
14	10	0.02	14.0	237	6.0

Table 9: Percentage Removal Efficiency

pH	TDS (%)	EC (%)	pH (%)	ORP (%)	COD (%)
2	94.9	89	54.02	-34.57	42.80
5	98.7	98	-14.94	-31.2	50.00
8	99.3	98	-83.90	-30.16	50.00
14	99.3	98	-2.21	-32.40	57.14

PHYSICOCHEMICAL PROPERTIES OF WASTEWATER

Effect of concentration on TDS, EC, pH, ORP and COD

The results of the physicochemical properties of raw wastewater and treated wastewater are presented in Table 1 and 2. The TDS for the wastewater after treatment were 20 ppm, 310 ppm, 5070 ppm and 2840 ppm it shows

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that increasing the concentration has no effect on TDS. After varying the concentration of treatment, TDS declined from 1590 to between 20 and 310. It also shows that 2.5 ml and 5 ml concentration is the best for reducing TDS which lies below the standard limit of TDS for treated wastewater. Increase in TDS value after increasing the concentration might be due to partial dissolution and possible interaction between the MgO-NP and the adsorbate.

Effect of concentration on EC (Electrical conductivity)

The result of the untreated wastewater for EC is 1.0, after treatment it shows a decline in the values. It reduced to 0.03, 0.44 and 0.09 and on increasing the concentration to about 20 ml, EC value increased above the raw wastewater which shows that increasing the concentration of the wastewater may lead to increase in the conductivity of the wastewater.

Effect of concentration on pH

Untreated wastewater has a pH value of 4.35 increasing the concentration of the wastewater lead to decline in pH to between 3.92 and 1.67 of the treated wastewaters. Further increase in the concentration led to increase in pH value of the treated wastewater. The above values fell below the WHO standard (5.0 - 6.0) for treated wastewater.

Effect of concentration on ORP (Oxidation-Reduction Potential)

Increasing the concentration led to an increase in the ORP value of the treated wastewater which might be as a result of the presence of an oxidizing agent in the adsorbent or wastewater

Effect of concentration on COD

The effect of adsorptive treatment on concentration is presented in Tables 2. An initial concentration of 14.00 mg/l was documented for COD at varying constant concentration of 2.5ml, 5ml, 10ml and 20ml. The COD concentrations recorded after each treatment for were 7.00, 3.00, 8.00, and 8.00mg/l. The results recorded were below the WHO (world health organization) and NESREA (National Environmental Standards and Regulations Enforcement Agency) environmental limits of 30 mg/l. The percentage removal efficiency calculated for the respective COD concentrations was 50, 78.5, 42.85 and 42.85.

Effect of Adsorbent Dosage

Effect of adsorbent dosage on TDS, EC, pH and ORP is shown in table 6 adsorbent dosage has no effect on TDS removal while for EC increasing adsorbent dosage has effect on removal of EC with removal efficiency of 90% pH removal efficiency is 95% increasing adsorbent dosage has effect on pH removal

Results presented in Table 3 shows that increasing adsorbent dosage will influence COD removal efficiency at an optimum contact time of 60 minutes. The percentage removal of 5.71, 5.71, 1.28 and 100 % on application of corresponding adsorbent masses of 2, 4, 6, 8 and 16mg, COD at an initial concentration of 14.00 mg/l was studied, with the result presenting the effect of adsorbent dosage on COD removal; percentage removal efficiency recorded ranged from a minimum of 5.71 to a maximum of 100 % at an initial concentration of 14.00 mg/l. Hence, the adsorption become constant and additional adsorbent made significant contribution.

Effect of pH

The result of TDS, EC, pH and ORP of treated wastewater is presented in Table 6 increasing the pH led to decrease in TDS of treated wastewater which is below the WHO limits for discharge 2000mg/l for EC increase in pH lead to decrease in EC of treated wastewater for ORP increasing the PH led to increase in the value of ORP which could be as a result of present of oxidizing agent in the adsorbent or sample.

In this experiment, pH of the solution plays a crucial role to determine the entire adsorption process, here the PH effect on the adsorption performance is related to the chemical structure of both adsorbent and pollutants. Thus, the optimization has been carried out to achieve the maximum adsorption. Moreover, a variation of PH results in the change of adsorbent surface.

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Therefore, studies were conducted within a PH range of 2-14 for the optimum removal of contaminants it was observed that the adsorption process is higher in the case of acidic medium pH 2 and decreasing on increasing the pH, suggesting acidic medium is favorable condition for the adsorption process in COD removal

Effect of time

Lower time has greater TDS removal capacity as compared to higher time of 80 min in Table 5 it is clear that the highest TDS removal takes place at lower time of 10 min. EC removal takes place at lower time, pH removal at lower time has high removal efficiency of 58 6% increasing contact time has no effect on pH removal ORP increase in time has high removal on ORP

COD adsorption is affected by time as shown in Figure the adsorption process was performed with a time range of 10-80 minutes at dosage of 50mg and concentration of 50ml as shown in Fig. Adsorption shows a rapid increase with increase in contact time. The kinetics of adsorption was fast and constant for 20 -80 minutes. The percentage contaminant removed are 57.14, 71.42, 71.42 and 71.42 for COD

CONCLUSION

This work has demonstrated the feasibility of synthesizing an eco-friendly adsorbent from aqueous extracts of locust beans and its application in reducing COD from tan liquor. Characteristics for the adsorptive potential of the adsorbent were evaluated and documented as having properties favorable for the removal of COD from tannery wastewaters. Application of MgO nano powder as an adsorbent for COD removal and its resultant efficiency shows great potentials while indicating the economic viability of diversifying the usability of locust beans extract. The results also implicate the tannery wastewater as a large reservoir of COD whose concentration does not satisfy the legal ranges for investigated parameters.

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