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# TANNERY WASTEWATER TREATMENT USING *JATROPHA CURCAS* AS BIO-COAGULANT AND BIOSORBENT

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## ABSTRACT

***Recently, attention has been focused on the activities of plant extracts that have been researched as green alternatives to chemical substances in treating turbid and toxic industrial wastewater. The use of Jatropha curcas as a bio-coagulant and metal-chelating agent for treating tannery wastewater has been scarcely exploited and documented. Effluent streams from tanneries are laden with pollutants ranging from suspended and dissolved solids to heavy metals. This study used protein extract from Jatropha curcas seed cake to treat tannery wastewater. 1 M sodium chloride solution was prepared, and protein was extracted from Jatropha curcas seed cake for active coagulation and metal complexing. The effect of treatment on pH, conductivity, and total dissolved solids (TDS) of the wastewater was obtained for coagulant dosages from 10 to 50 ml/L for a retention time of 24 hr. The pH of the treated effluent shifted towards alkalinity while conductivity and TDS increased as coagulant dosage increased. The pH, conductivity and TDS of the treated effluent were within acceptable limits by NESREA and WHO. The reduction in concentration of selected metals – chromium, iron, magnesium, calcium, sodium, and iron- was obtained and analysed via atomic absorption spectroscopy. Jatropha curcas seed cake extract proved to be an active bio-coagulant and metal chelator for treating tannery wastewater.***

## KEYWORDS

*Jatropha curcas*, protein extract, tannery wastewater, coagulation, sedimentation rate, metal sorption.

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## INTRODUCTION

Recently, using natural coagulants (bio-coagulants), which are biodegradable and environmentally friendly, has been a reliable route in alleviating the problems associated with conventional synthetic coagulants. Such disadvantages include high cost, limited availability (Zurina *et al*., 2011), and residual monomers that possess strong carcinogenic properties and lead to neurotoxicity (Vijayaraghavan *et al*., 2011). Bio-coagulants are useful for water clarification and have antimicrobial and heavy metal removal properties in some instances (Choy *et al*., 2015). According to Basra *et al*. (2014), the aqueous extract from these plant seed powders has been more effective than the seed powder in removing lead and chromium from sewage waters via the amino acids present in them.

Plant protein extracted using 1.0 M sodium chloride solution has also performed better in extracting active coagulants than fresh or distilled water (Bouchareb *et al*., 2021). *Jatropha curcas*, commonly called physic nut, has been used in several areas, including biodiesel production, medicinal purposes, as a live fence to deter animals and in soap production. The ripe seeds are depicted pictorially in Plate 1. Predominantly, the oil extracted from *Jatropha curcas* seed has been useful as a raw material for biodiesel production, leaving the seed cake to minimal use. This work thus investigated the capability of the protein extract from *Jatropha curcas seed* cake to reduce the pollution load of the combined effluent streams through coagulation.

**Plate 1:** *Jatropha curcas* seeds

Earlier works suggested that the adsorption and charge neutralisation mechanism rules as the main mechanisms of coagulation using *Jatropha curcas* seeds as for other plant proteins (Abidin *et al*., 2011; Zurina *et al*., 2011; Vijayaraghavan *et al*., 2011; Ndbigengesere *et al*., 1995). This mechanism involves the adsorption of an oppositely charged coagulant on the colloidal surface. The colloidal particles are usually negatively charged under normal surface water conditions.

Hence, positively charged coagulants will be attracted towards the colloids, resulting in surface charge neutralisations (Choy *et al*., 2015). Figure 1 illustrates the regions of charge attraction, which have patches of positive and negative regions. Breakage reversibility for adsorption and charge neutralisation is usually reversible as *van der Waals* forces with weak floc strength can happen anytime, leading to higher floc recovery.

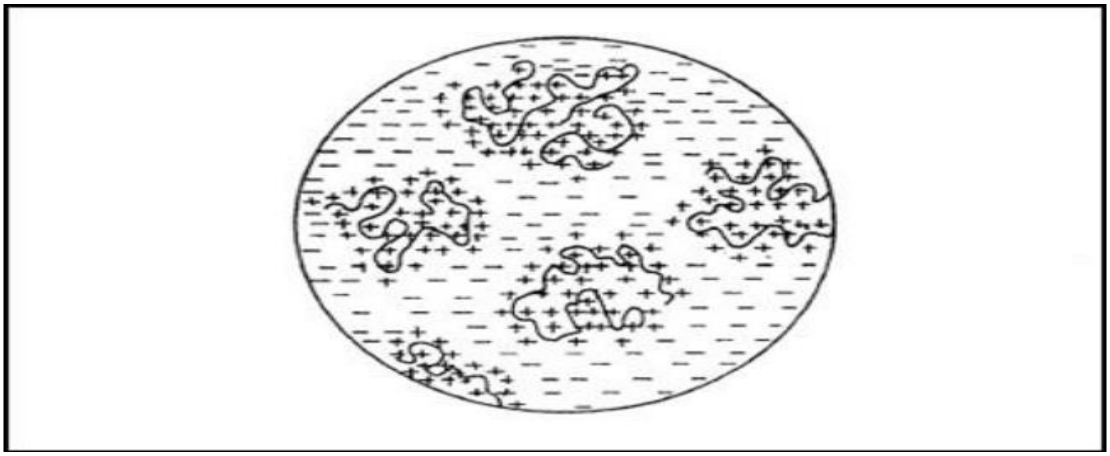

**Figure 1:** Electrostatic patch in charge neutralisation mechanism (Tripathy and De, 2006)

The active coagulating agents in *Jatropha curcas* are proteins of polar nature that dissolve well in polar solvents such as water. Meanwhile, the toxic phorbol ester compounds will not dissolve in water but remain in the seed cake. While numerous studies have utilised plant extracts for turbidity removal, commercialisation and industrial applications are still lacking. Furthermore, the *Jatropha curcas* plant has been reported to be active in the uptake of heavy metals like $Cr^{3+}$ from soils (Akintola *et al*., 2019; Parisa *et al*., 2010).

Low molecular weight ligands found in *Jatropha curcas* seeds, such as Cysteine, have been shown to enhance metal uptake in salt water as against freshwater due to low Calcium levels in salty (marine) water (Fengjie *et al*., 2019). Generally, studies have shown that seeds can adsorb metal ions and highly toxic compounds (Apori *et al*., 2020; Ravikumar & Sheeeja, 2013). This work used *Jatropha curcas* seed cake extract to treat tannery wastewater. The efficacy of this natural coagulant will thus be heightened with the best results of both the pH and coagulant dosage used and the metal reduction potential.

## MATERIALS AND METHODS

### Sourcing of materials and Preparation of coagulant agent

Wastewater was collected from a tannery in Kano, Nigeria, within 24 hours. *During the dry season, Jatropha curcas were obtained from a local market in Hunkuyi, Kudan Local Government Area, Kaduna State, Nigeria*. The outer shell was removed manually from a selection of good-quality seeds. Using an electric blender, the kernel was ground to a fine powder (63–500µm).

To prepare the coagulant, the oil was extracted from the seed using soxhlet extraction and n-hexane as a solvent to obtain the seed cake. Then, 5 g of the *Jatropha seed* cake was blended with 100 mL of 1 M sodium chloride solution at 35 ℃ for two minutes to extract the active ingredients from the *Jatropha* seed cake (Zurina *et al*., 2013).

The resulting suspension was filtered through a muslin cloth. High-Performance Liquid Chromatography was used for protein separation analysis to determine the amino acids present in the extract. The technique uses a liquid mobile phase responsible for separating the sample components that will flow through a column and provide data on the compounds' separation, as Shemishere et al. (2018) reported. The various types of amino acids, such as Proline, Arginine, and Cysteine and their concentrations were revealed via this analysis.

### Main coagulation experiments

The coagulation test was carried out in several batch processes using a magnetic stirrer (78HW-1 Searchtech, USA). This involved three steps: rapid mixing (for 2 mins), slow mixing (for 10 mins), and sedimentation, conducted in batch processes over 24 hours.

After the sedimentation, the supernatant from each sample was collected to measure the pH, conductivity and TDS using a Jenway Conductivity Meter Model 4510. The effects of pH and coagulant dosage on the coagulation process's physicochemical properties and sedimentation rates were investigated. All the experiments were repeated twice.

**Sample Digestion for Heavy Metals Analysis**

Heavy or trace metals were determined after the digestion of the samples. Water sample digestion was done by taking 10 ml of the sample and adding 4 ml perchloric acid, 20 ml concentrated nitric acid and 2 ml concentrated tetraoxosulphate (VI) acid. This was digested using Aluminium block digester 110. The mixture was heated until white fumes evolved and a clear solution was obtained.

After digestion, the samples were allowed to cool and then transferred to a 100 ml volumetric flask. This was made up to 100 ml with distilled water and thoroughly mixed.

The samples were allowed to stand overnight to separate insoluble materials. Filtration was done through a 0.45 μm Millipore type filter. Iron (Fe), Chromium (Cr), Calcium (Ca), Sodium (Na) and Magnesium (Mg) were determined using Unican 929 Atomic Absorption Spectrometry in parts per million. The analysed metals were selected based on those eminent in the tanning process streams. The results are compared and discussed in Figures 4 and 5.

## RESULTS AND DISCUSSION

Preliminary Physicochemical analysis was taken on the untreated tannery wastewater, as shown in Table 1.

**Table 1:** Physicochemical analysis of untreated tannery wastewater

| Physicochemical Analysis | Initial Values |
|---|---|
| Colour | Brownish – Green |
| pH | 7.3 |
| Conductivity | 230 $\mu Scm^{-1}$ at $26^{0}C$ |
| Total Dissolved Solids | 150 mg/L at $26^{0}C$ |
| Turbidity | 408 NTU |

Other initial values of the metals are shown in Figures 4 and 5 and compared with those after metal uptake.

The amino acid analysis is shown in Table 2 for *Jatropha curcas* seed cake extract (JC).

**Table 2:** Amino acids analysis for *Jatropha curcas* seed cake extract (JC)

| Amino Acids | JC |
|---|---|
| Proline | 11.26213 |
| Cysteine | 44.61758 |
| Asparagine | 13.41159 |
| Arginine | 25.48188 |
| **TOTAL** | **94.77318** |

Generally, these amino acids provide more functional groups and a strong affinity for heavy metal ions over a wide pH range (Verma *et al.*, 2017). The pH of the solution was decreased when the extract was introduced into the wastewater containing heavy metals, which can be attributed to their protons being exchanged against the metal ions as a metal chelating agent (Zaroual *et al.*, 2014).

Proline, found in the protein extract, functions as an osmoticum that detoxifies the heavy metal stress effects on the cytoplasm of plants (Aslam *et al*., 2017). It does this by forming complexes with metal species, reducing their toxic effect on plant species. Several authors have studied this ameliorating effect of Proline with several metals (Hayat *et al*., 2021; Aslam *et al*., 2017).

Cysteine was the highest in *Jatropha curcas* seed cake extract (JC). It has been established to be a heavy metal chelator, as reported by various authors who studied its use in Mercury reduction from plants and contaminated soils (Yeon-Ok *et al*., 2022; Aysin *et al*., 2020) and in Chromium reduction (Terzi *et al*., 2021). Arginine, also found in *Jatropha curcas*, effectively removes heavy metals from water samples, as Verma *et al*. (2017) reported.

All of these amino acids were employed in the metal uptake of Chromium (Cr), Iron (Fe), Calcium (Ca), Magnesium (Mg) and Sodium (Na) from the collected tannery wastewater without adjusting pH.

**Effect of pH on turbidity, TDS and conductivity**

The effect of pH was studied by adjusting the tannery wastewater pH values at 3, 5, 7, and 9, and the coagulation test was performed at room temperature using coagulant dosages of 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L and 50 mg/L. The pH of the wastewater was adjusted using 0.1 M NaOH and 1 M HCl solutions.

During the experiments, big flocs were observed, especially for samples at pH 3, which was reported also by Zurina *et al*. (2011). As an amphoteric molecule, the pH is sensitive to the charge on the *Jatropha curcas* seed cake protein. Nevertheless, turbidity reduction was most efficient at pH 3 and 11, with the best results at pH 11 giving percentage reduction values ranging from 85 – 90 % for various coagulant dosages. This is in agreement with Zurina *et al*. (2011). Above pH 11, the amino acids, except arginine, exhibit negative charges. However, according to Makkar *et al*. (1997), arginine makes up a large percentage of the total protein present in *Jatropha curcas.* Therefore, this arginine is active in coagulation at a pH of 11 and higher.

Figures 2 and 3 similarly observed that the coagulation was more favourable at an acidic pH of 11 with the highest TDS and conductivity values of 979 mg/L and 1653 μScm$^{-1,}$ respectively, at these points. The results showed that the treatment increased the acidic ranges towards alkalinity and reduced the alkaline ranges towards acceptable pH ranges (between pH 6.5-9.5). This can be explained by the proton acceptance of the essential amino acids in the coagulant protein when dissolved in water, releasing a hydroxyl group and making the solution essential (Daniyan *et al*., 2011). Conclusively, for optimum results using coagulant from *Jatropha curcas* seed cake extract, the wastewater may require pH adjustment before coagulation.

**Effect of coagulant dosage on turbidity, TDS and conductivity**

For studying the effect of coagulant dosage, the tannery wastewater pH was fixed at several values where the maximum TDS and conductivity were obtained, while coagulant dosage was varied at 10 ml/L, 20 ml/L, 30 ml/L, 40 ml/L and 50 ml/L. Larger flocs were seen to form with increasing coagulant dosage, and the final wastewater after treatment was more apparent than the initial. From the study, the best turbidity reduction of 90 % at pH 11 was obtained at a coagulant dosage of 30 ml/L, followed by 88 % at a 50 ml/L dosage.

From Figures 2 and 3, conductivity and TDS increased as coagulant dosage increased. This led to maximum TDS and conductivity readings at the highest coagulant dosage of 50 ml/L.

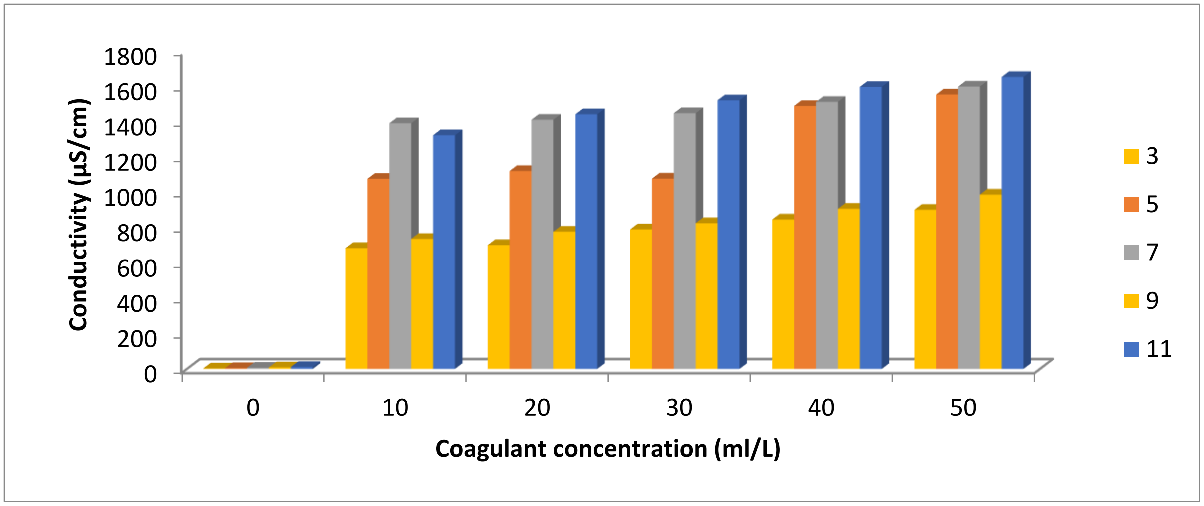


**Figure 2:** Variation of conductivity with coagulant concentration and pH

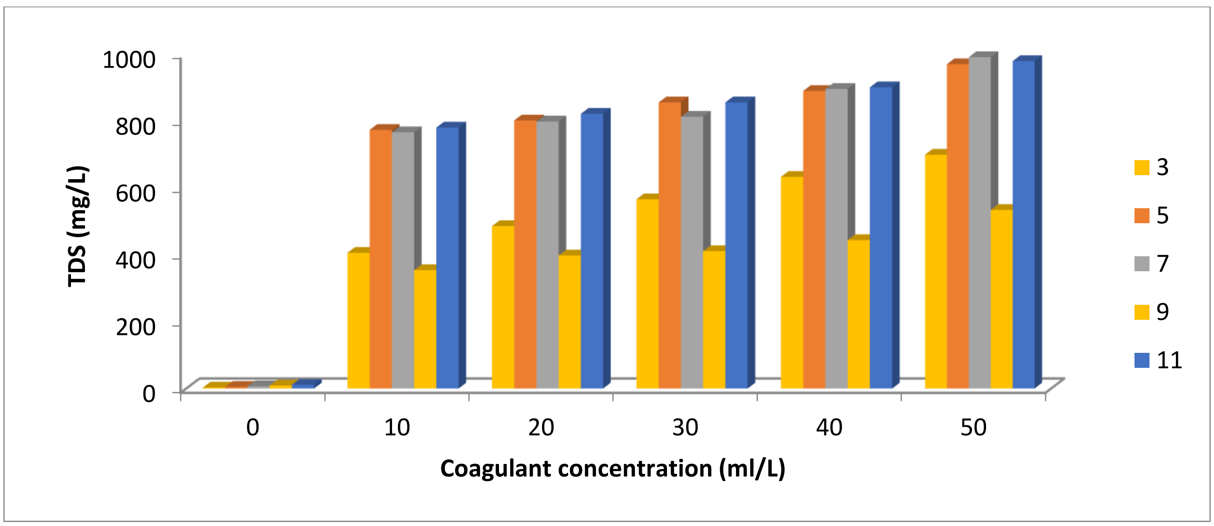


**Figure 3:** Variation of TDS with coagulant concentration and pH.

The declared turbidity removal for safe drinking water is 5 NTU. The lowest turbidity value achieved was 40 NTU, which is still above acceptable drinking water limits. Nevertheless, the treated wastewater can be re-used for other industrial applications within the leather industry. The total dissolved solids (TDS) describe the inorganic salts and organic matter in a water solution. The acceptable limit of TDS in water is less than 1200 mg/L compared to the maximum value of 979 mg/L obtained from this study.

On the other hand, conductivity does not directly impact human health. However, high conductivity can lead to corrosion in pipes in industrial use and lead to the elimination of plants. Conductivity values between 800 and 2800 $\mu Scm^{-1}$ are fair, which is unacceptable by NESREA (2011) and W.H.O. (2011). The 1653 $\mu Scm^{-1}$ obtained from this study is thus within acceptable limits. NESREA (2011) and W.H.O. (2011) stipulate these turbidity, TDS and conductivity limits. Figures 4 and 5 illustrate the effect of the Jatropha curcas seed extract on reducing or increasing the concentration of selected metals via AAS and measured in ppm.

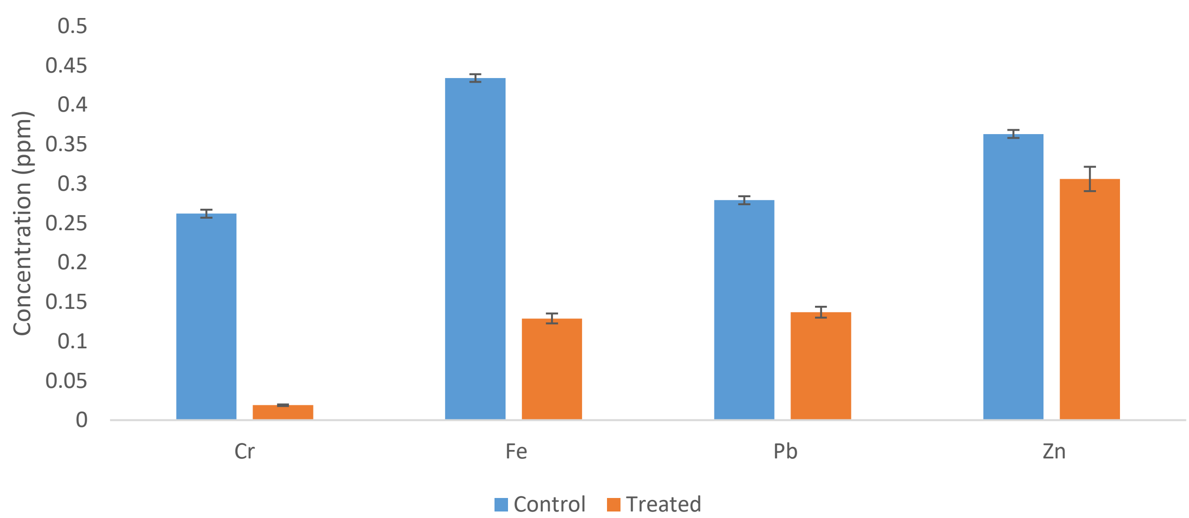


**Figure 4:** Reduction in concentration of metals

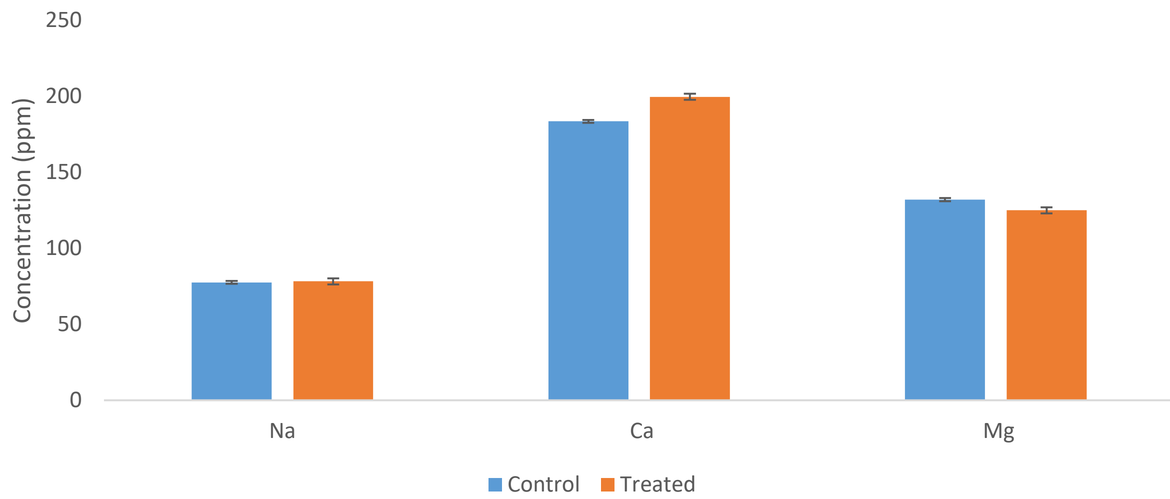


**Figure 5:** Concentration of nutritive elements before and after treatment

Using *Jatropha curcas* seed cake extract (JC), a reduction in Chromium concentration of 92.75% was achieved, a reduction in Iron concentration of 70.28%, a reduction in Lead concentration of 50.91% and a reduction in Zinc concentration of 15.70% was achieved. This is attributed to the concentration of active amino acids and organic acids in plant extracts.

There is an associated complexing of Cysteine with calcium, as reported by Fengjie *et al*. (2019). Nevertheless, *Ugbogu et al. (2013) reported Jatropha curcas seeds as* a rich source of Calcium, leading to higher calcium levels than lower values in Figure 6.0. An increase as opposed to the afore-discussed reduction in some other nutritive elements like sodium 0.90% and calcium 8.09% was attributed to the plant's inherent rich deposit in the concentration of some desired metals (Magu *et al*., 2018; Ugbogu *et al*., 2013; Azza and Ferial, 2010).

From these results, *Jatropha curcas* proteins were observed to function as active natural metal chelators in this study, suitable for the treatment of water containing undesirable heavy metals in substantial concentrations as supported in studies by Gallegos Tintoré *et al*. (2011) and Zaroual *et al*., (2014).

## CONCLUSION

From the results obtained, the maximum values for TDS and conductivity were observed at a coagulant dosage of 50 ml/L and wastewater pH of 3. The best turbidity reduction of 90 % was achieved at pH 11 and a 30 ml/L coagulant dosage. Further study will target reducing sodium chloride concentrations for protein extraction. This reduction may help decrease the TDS and conductivity values so they can fall within drinking water ranges. The protein extract also reduced heavy metals like Chromium and Lead by 92.75% and 50.91%, respectively. All metal concentration values in treated wastewater were lower than NESREA (2011) and WHO (2011) standards. *Jatropha curcas* seedcake protein extract thus has great potency for an eco-friendly, economical wastewater treatment technology for tanneries. Further improvement in the efficiency of this technology should be investigated. Also, commercialisation and industrial applications should be exploited.

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