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Treatment of Electroplating Industry Wastewater by Electrocoagulation using *Moringa oleifera* Seeds as a Natural Coagulant

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Abstract

The quality and accessibility of drinking water is chief importance to human health. The main objective of this work was to use *Moringa oleifera* seeds as a natural coagulant in electrocoagulation process for the treatment of electroplating industry wastewater. It has been found that *Moringa oleifera* is the best bio coagulant which can replace aluminum sulphate (alum). The efficiency of *Moringa oleifera* seed cake in removing heavy metals ions such as chromium, copper, zinc, cobalt and lead from the wastewater sample by means of jar test followed by electrocoagulation process was very much reliable. The removal of heavy metal ions observed for *Moringa oleifera* seeds treated water were 79% for lead, 50% for copper and zinc, and more than 90% for chromium and cobalt, at an optimal dosage of 200 mg/L. Around 90-96% of turbidity has been reduced from the wastewater by *Moringa oleifera* seed cake, though it has a no glaring effect on the pH which is also an advantage. The *Moringa oleifera* seed treated water has been taken for the further treatment by electrocoagulation process. Concluding that, the rate of removal of pollutants linearly increased with increasing doses of seed cake. During electrocoagulation process the heavy metals like cobalt and lead was completely removed from the water sample and other heavy metal ions such as chromium, copper and zinc concentration in water sample has met the level of water standards of WHO (World Health Organization).

Keywords: Adsorption; Biosorption; Ion-exchange

Introduction

Water is the most important resource on the planet Earth, and it is the essence of all life on earth. But due to some certain human activities this resource is getting scanty in its pure state. The main reason for contamination of water is due to uncontrol population and unplanned industrial growth. The water is said to be uniquely vulnerable to pollution known as 'Universal solvent' water can dissolve more substances than any other liquid on earth. The electroplating industry is one of the major industries which produces immense portion of wastewater containing heavy metals. The presence of heavy metals in water is a great threat to human beings and environment. Various techniques have been implemented for the treatment of heavy metals, including precipitation, adsorption, biosorption, ion-exchange, electrodialysis and membrane separation. Precipitation is the one of the most suitable among these techniques and is the most economical. It is based on chemical coagulation in which chemical coagulant are used such as aluminum and iron salt to remove colloidal matter as hydroxides from wastewater. Although, it is very efficient in treating industrial effluents, but the use of chemical coagulation may produce secondary pollution due to the added chemical substances. This drawback, together with the need for low cost-effective treatment of wastewater, encouraged many studies on the use of electrocoagulation for the treatment of several industrial effluents [1]. In this study to treat electroplating wastewater a combined process was used in which a nontoxic organic coagulant (*Moringa oleifera* seeds) was used before the electrocoagulation process Mpagi Kalibbala et al. [2].

The process electrocoagulation for the treatment of wastewater has recently attracted great attention. It has found to be very effective to treat textile wastewater, electroplating wastewater, slaughterhouse wastewater and tannery wastewater. The passing of an electric current through water has proven very effective in the removal of contaminants from water. The application of current leads to the generation of hydroxide ions at the cathode. The generated flocs which allows the pollutant to settle down and can be easily removed by sedimentation. During an electrocoagulation process, the anions and salts content will not increase in the water sample, compared with chemical metal precipitation [3]. This contributes to the production of metallic sludges which are compact as compare to those generated by chemical precipitation. Moreover, electrocoagulation process requires simple equipment, small retention time and it is easy to operate. These features contribute to the reduction of operating cost for industrial applications [4].

Moringa oleifera (MO) seeds, a non-toxic tropical, drought-tolerant tree, available throughout the year found in India, sub-Saharan Africa and Latin America. It is a multipurpose tree used for food and has numerous industrial, medicinal and agricultural uses, including animal feeding it is commonly known as tree of life [5]. Among many other properties *Moringa oleifera* seeds contain a coagulant protein that can be used for treatment of wastewater. The protein act as a cationic polyelectrolyte which attaches to the soluble particles and creates binding between them leading to large flocs in the water [6,7]. *Moringa oleifera* seeds are the best natural coagulant that can replace aluminum sulphate (alum), and it does not have any disadvantages such as high cost and pH alteration that have been exhibited by using chemical coagulant. *Moringa* has also been proven to produce significantly less sludge as compared to Aluminum Sulphate (alum), which is an advanced advantage especially if the sludge is to be dewatered are treated in some other way before it is disposed of to any water bodies or land. This natural coagulant is biodegradable, environmentally friendly and non-toxic, thus, making it a potentially viable substitute to alum in addressing the challenges facing potable water supply especially in rural and peri-urban areas of developing countries [8,9]. This study aims to investigate different parameters of water sample such as; COD, TDS, salinity, conductivity using different concentration of MO seed cake followed by electrocoagulation for the treatment of Electroplating industry wastewater from Surajpur industrial area to understand the coagulation property of MO seeds and also its application for removal of heavy metals.

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Materials and Methods

Sampling site

The wastewater sample used in present study was collected from an electroplating industry in Greater Noida, Surajpur Industrial Area, India. The typical qualities of raw electroplating wastewater all listed below in Table 1.

Oil Extraction of MO seeds

Extraction of the oil was done by removing MO seed pod shells and the kernels were grounded using a domestic blender and was sieved through 600-micrometer sieve. The oil from the powdered MO seeds was removed with the help of hexane. The MO seed powder and hexane was mixed for 30 min, using magnetic stirrer and was filtered through a Whatman filter no. 40. The remaining solids in the filter (press cake or seed cake) were dried at room temperature for 24 hours. The stock solution was prepared by adding different concentration of seed cake (50, 100, 150 and 200 mg) into distilled water. To avoid ageing effect a fresh solution was prepared every day for different concentration. Some studies show that the coagulation efficiency of MO seeds decreases with increase in duration of storage seeds, however the coagulation efficiency is independent of storage temperature and container. To obtain a proper treatment efficiency the duration of seed should not exceeds 24 hours [10].

Experimental device for electrocoagulation

The process electrocoagulation was carried out in 1000 mL beaker using vertical potential electrode. The setup has two iron rods one serving as a cathode and the other as anode. The spacing between the electrode is 40 mm and of size 10 cm*4 cm. The electrode is connected to a DC power supply (APLAB regulated DC power supply L6403). During electrolysis, the positive side undergoes anodic reactions, while on the negative side, cathodic reaction is encounteted. Consumable metal rod, such as iron, was continuously producing ions in water. The released ions neutralize the charges of particles and thereby initiate coagulation.

Wastewater treatment by MO seeds

To determine the efficiency of MO seeds as a coagulant for the treatment of wastewater by using a PB-700 6 Paddle jar test apparatus. Each beaker was labelled and was filled with 1000 mL of raw water with identical turbidity level; the coagulant dose of different volumes was put into each beaker using pipettes from the stock solution and operated with initial speed of 120 rpm for 3 min. Then the stirring rate was lowered to 40 rpm and this rate was kept for 17 min. The paddles were stopped completely, and the beakers were left for 45-55 minutes sedimentation [5]. The coagulation took place and the floc settle at the bottom leaving the transparent medium at top due to the presence of water-soluble cationic coagulant protein. The most optimally purified water at selected dosage was transferred into another beaker for electrocoagulation.

Parameters	Value	Parameters	Value
pH	1.75	Chromium (mg/L)	112.308
COD (mg/L)	521.09	Zinc (mg/L)	96.52
Turbidity (NTU)	65.3	Copper (mg/L)	26.521
Salinity (ppm)	8.97	Cobalt (mg/L)	3.077
TDS (ppm)	9.82	Lead (mg/L)	1.996
Conductivity (μS)	16.1	Sulphate (mg/L)	170.1

Table 1: Pre-treatment of MO seeds: Typical qualities of raw electroplating wastewater.

Treatment by electrocoagulation

The process electrocoagulation was performed on the most optimally purified water after treating the wastewater by MO seeds, at a constant current voltage of 8.0V and at pH 8.15. Before experiment, electrode was properly scraped with sandpaper to remove any scale and then cleaning it by dipping in 1N sulfuric acid solution and distilled water in order to ensure the homogenous solution. The reactor was placed under the magnetic stirrer and stirred at a rate of 200 rpm throughout the experiment to allow the precipitate to grow large enough for removal. Later, the samples were collected at 10 min time intervals, and filtered using Whatman's filter paper. The collected samples were taken to analyze its different parameters.

Measured parameters

Turbidity measurement: The turbidity was measured with a 2100P turbidimeter from Hach and the water sample was compared before and after the treatment.

COD measurement: The instrument used for measuring the COD value was DR 2800 spectrophotometer. The sample was prepared by adding about 2 mL of the water sample before and after the treatment was pipetted into COD reagent vials, along with 1.5 mL potassium dichromate (strong oxidizing agent) which oxidizes organic matter was inserted into a COD digestor. The sample was heated for 2 hours at 15°C.

Electric conductivity, pH, and salinity, TDS, DO: A multi-function PCD 650 water-proof portable meter was used to measure the electrical conductivity, salinity, pH, TDS, DO.

Heavy metal removal measurements: To determine the concentration of heavy metals present in wastewater sample foregoing to and after treatment, a perk-in Elmer an Analyst 800 high performance Atomic Absorption Spectrometer (AAS) was used. A series of calibration solution such as chromium, zinc, copper, cobalt and lead were prepared from standard stock solution (1000 mg/L). Each metal was prepared at different concentration from 0 to 6 ppm. The water sample was digested on a hot plate before analyzing the concentration of heavy metals [9].

Sulphate measurement: A DR 5000 UV spectrophotometer was used to measure the sulphate, about 20 ml of buffer solution was added from stock solution (containing 30 gm magnesium chloride, 5 gm sodium acetate and 20 ml of acetic acid) in 50 ml of wastewater sample for the measurement.

Results and Discussion

Oil extraction

The oil was extracted using n-Hexane to procure seed cake. The extraction of oil present in MO Seeds were necessary because it will affect the coagulation and heavy metal removal activities; on that account MO seeds with high oil content would have negative impact on the wastewater treatment process [11].

Electrode material and electrode cleaning

The electrodes used in this study was, the Fe-Fe electrode combination (iron-iron combination). This combination has the maximum heavy metal removal efficiency due to iron oxide effective adsorption capacity. To enhance the efficiency of electrode the electrode were properly scraped with sand paper to remove any scale and cleaning the electrode by dipping it in the solution of 1N sulfuric acid and distilled water, using the electrode without cleaning them prior to every experiment will led to decrease the removal efficiency of electrodes due to passivation with time which results in less generation iron during electrocoagulation process [12].

Effect of operating time and pH

The operating time was investigated at current voltage of 8 volt from 10 to 50 minute. The maximum efficiency of electrocoagulation process was obtained at a treatment time of 30 minutes, and a further increase in treatment time did not result in any significant improvement in removal efficiency of the studied parameter. The pH is an important factor influencing the performance of electrocoagulation process. Usually, the pH of the medium changes during the operating process and this change depends on the type of electrode material and on initial pH of the water sample. The increase of pH at initial pH is lower than <2 are attributed to the hydrogen evolution and result in an increase of the concentration of OH ions at the cathodes. The studies show that the removal rate of heavy metals by electrocoagulation process was increased with the increase in pH [13].

Heavy metals removal by MO seeds

The concentration of heavy metal present in wastewater sample at initial stage of Cr (112.308 mg/L), Zn (96.520 mg/L), Cu (26.521 mg/L), Cb (3.077 mg/L), Pb (1.996 mg/L). The presence of high concentration of heavy metals are typically associated with severe environment and health effects [14]. For reducing heavy metals concentration from wastewater sample MO seed cake were used as a coagulant, adsorbent and antimicrobial agent [15,16]**.** Due to the removal of oil from MO seed, the polyelectrolyte protein was activated and combined with the heavy metals leading to complex formation. The polyelectrolyte is unchain due to the extraction of oil since it is not soluble in the lipid [6]. The current studies show that, the heavy metals removal efficiency was increased by increasing the concentration of MO seed cake for the electroplating industry wastewater sample. Vikashni et al. [9] have reported that the removal efficiency for copper (Cu) and chromium (Cr) was up to 90% and 50% using MO seed cake. The concentration of copper was similar with what was found in by Vikashni et al. [9], but in the case of chromium the removal efficiency was more than 90% after the treatment, concurring to the studies of Ali et al. [17] and contradicting the studies of Vikashni et al. [9]. The percentage of cobalt (Cb) removed from the wastewater sample after treatment was 96%, amount of zinc (Zn) removed from the wastewater sample was up to 50% completely agreeing with Vikashni et al. [9], although zinc is an essential element needed for human body in small amounts but if its concentration is slightly more than the permissible limit in water it will affect the human health severely [18]. The removal of lead was not that much satisfying although its concentration was not that high as compared to other heavy metals, the amount of lead (Pb) removed was 79% after the treatment, which is like the studies of Sajidu et al. [19] and Subramanium et al. [20]. The removal percentage of Pb in their studies was 89% and 80% respectively (Table 2 and Figure 1).

Removal of heavy metals from MO seed treated water by electrocoagulation

After treating the wastewater sample by MO seed cake at different concentration, the most optimally purified water sample was taken for electrocoagulation process. The percentages of heavy metals present in water were shown in Tables 3-6, Figures 2-5.

Result for different parameters

The current studies show that the pH of electroplating wastewater sample did not changed after treating the water sample with MO seed cake. The initial pH value was 1.75, but after treatment the pH value shows a very slight increment. This proved that MO seed cake is not affecting the pH Value in water samples, conceding with published observations Arnoldsson et al. [5] but it has shown a very promising effect on different parameter of wastewater sample like conductivity, salinity, TDS, turbidity, COD, DO.

Heavy metals	Initial	50 (mg)	100 (mg)	150 (mg)	200 (mg)
Cr	112.308	40	37.475	21.682	5.53
Zn	96.52	95.978	63.492	57.398	48.615
Cu	26.521	8.652	7.15	2.998	2.497
Co	3.077	2.665	1.734	0.972	0.098
Pb	1.996	0.634	0.484	0.426	0.41

Table 2: Heavy metals removal by MO seeds: The removal percentage of Pb in their studies was 89% and 80% respectively.

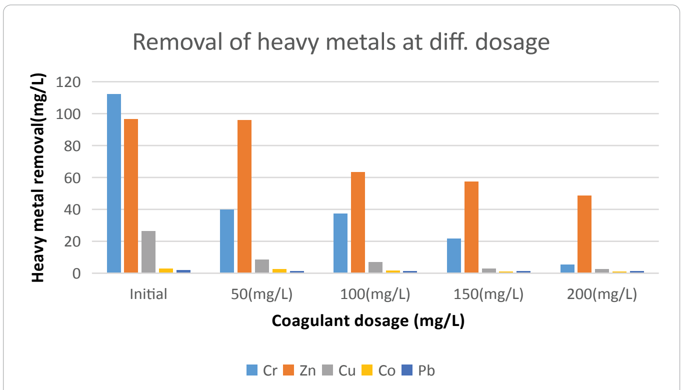

Figure 1: Removal of heavy metal at different dosage.

Heavy metals	Initial	10 min.	20 min.	30 min.	200 (mg)
Chromium	40	7.656	7.611	7.405	5.53
Zinc	95.978	2.311	2.297	2.135	48.615
Copper	8.652	0.49	0.473	0.438	2.497
Cobalt	2.665	0.293	0.212	0.211	0.098
Lead	0.634	0.046	0.033	0.031	0.41

Table 3: Electrocoagulation of 50 mg MO seeds treated water.

Heavy metals	Initial	10 min	20 min	30 min
Chromium	37.475	7.436	7.315	6.501
Zinc	63.492	1.66	1.427	1.429
Copper	7.15	0.496	0.411	0.375
Cobalt	1.734	0.267	0.133	0.117
Lead	0.484	X	X	X

Table 4: Electrocoagulation of 100 mg MO seeds treated water.

Heavy metals	Initial	10 min	20 min	30 min
Chromium	21.682	2.184	2.13	1.973
Zinc	57.398	0.972	0.944	0.759
Copper	2.998	0.286	0.116	0.112
Cobalt	0.972	0.052	0.048	0.048
Lead	0.426	X	X	X

Table 5: Electrocoagulation of 150 mg MO seeds treated water.

Heavy metals	Initial	10 min	20 min	30 min
Chromium	5.53	0.097	0.054	0.048
Zinc	48.615	0.474	0.194	0.06
Copper	2.497	0.08	0.07	0.07
Cobalt	0.098	X	X	X
Lead	0.41	X	X	X

Table 6: Electrocoagulation of 200 mg MO seeds treated water.

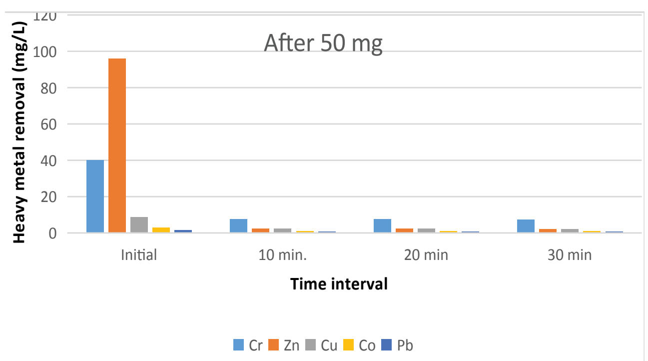

Figure 2: Heavy metal removal (mg/L): After 50 mg.

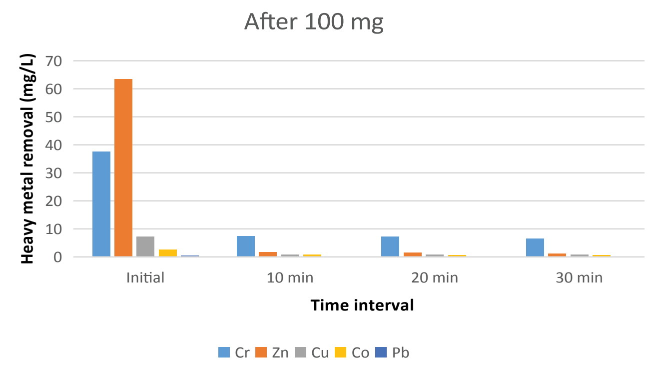

Figure 3: Heavy metal removal (mg/L): After 100 mg.

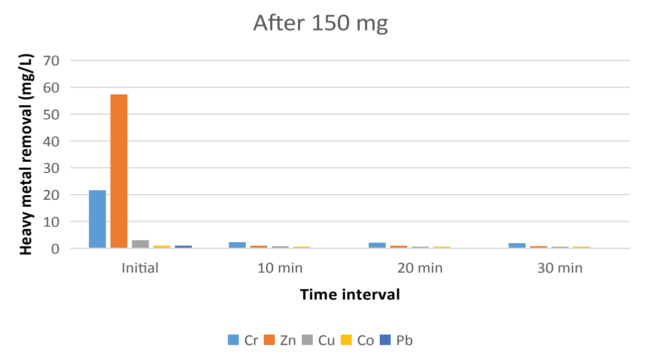

Figure 4: Heavy metal removal (mg/L): After 150 mg.

Conductivity value has been increased from 16.10 µS to 68 µS. The value of salinity also increased from 8.97 ppm to 23.90 ppm. The results obtained were similar with what was concluded by Arnoldsson et al. [5]. The value of TDS was decreased from 9.81 ppm to 5 ppm after treatment, completely agreeing with studies of Meenakshi et al. [12]. However, TDS result was not in agreement with Arnoldsson et al. [5] who stated that TDS was increased after treating the wastewater by MO seed cake. The initial COD of electroplating wastewater sample was 521.09 mg/L before treatment but increased to 641.54 mg/L after the treatment, this is due to the presence of oil content in MO seed cake which has not been removed completely. The factor which is also responsible for increase in the value of COD was due to the remaining organic matter present in the MO seed cake [5]. The initial value for turbidity of electroplating wastewater sample was from 65.3 NTU

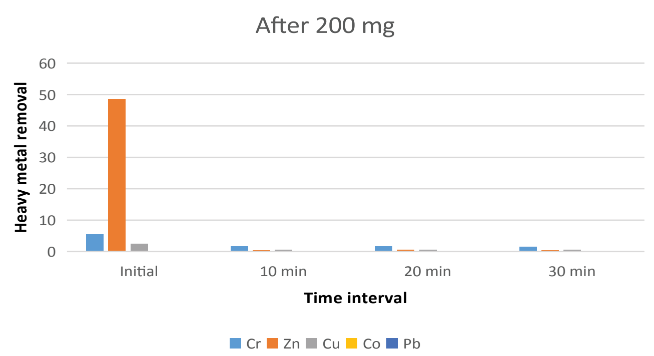

Figure 5: Heavy metal removal (mg/L): After 200 mg.

Parameters	Initial	50 mg/L	100 mg/L	150 mg/L	200 mg/L
pH	1.75	1.75	1.75	1.78	1.8
Turbidity (NTU)	65.3	7.36	6.27	4.08	2.31
Conductivity (µS/cm)	16.1	21	56	63	68
Salinity (ppm)	8.97	11.43	17.95	19.06	23.9
TDS (ppm)	9.82	7.67	7.08	5.98	5
COD (mg/L)	521.09	428.85	442.62	563.49	641.54

Table 7: Results for different parameters.

Parameters	Value at 200 mg/L	10 min	20 min	30 min
pH	1.8	7.3	7.81	8.15
Turbidity (NTU)	2.31	0.133	0.117	0.108
Conductivity (µS)	68	9.32	7.85	4.64
Salinity (ppm)	23.9	8.22	6.45	4.45
TDS (ppm)	5	5.08	4.98	2.97
COD (mg/L)	641.54	137.33	129.6	87.41
Sulphate (mg/L)	170.1	61	63	64

Table 8: Results for different parameters with time.

which decreases to 2.31 NTU, this shows that the removal efficiency of turbidity could be increased by using high concentration of MO seed cake [21] (Table 7).

After treating the wastewater sample by different dosage of *Moringa oleifera* seed cake, the most optimally purified treated water i.e., water treated with 200 mg/L *Moringa oleifera* seed cake has undergone electrocoagulation process. Due to electrocoagulation the pH has increased to 8.15. The value conductivity and salinity decrease from 68 µS to 4.64 µS, and 23.90 ppm to 4.45 ppm. TDS has reduced from 5.00 ppm to 2.97 ppm. COD decreases from 641.54 mg/L to 87.41 mg/L. The value of turbidity also decreases from 2.31 NTU to 0.108 NTU (Table 8).

Conclusion

This paper concluded that electroplating industry wastewater can be treated and reused by advanced method of electrocoagulation and using *Moringa oleifera* seeds as a coagulant, to evaluate the impact and optimize the different parameter levels related with this combined process in treatment of wastewater and in removal of heavy metals. *Moringa oleifera* seeds can be used in the coagulation process because it has a good coagulating property as compared to alum; result suggested that, the optimum dosage of *Moringa oleifera* seed cake was 200 mg/L as a coagulant to treat wastewater effectively. Turbidity was removed up to 90-96% after the treatment. Although there was no noteworthy change on the value of pH, However, the value of COD was increased due to the organic content present in the MO seed cake. Except that, *Moringa oleifera* seed cakes were successfully able to remove the heavy metals from the wastewater. More than 90% of Chromium (Cr) and Cobalt (Cb) was removed, whereas Copper (Cu) and Zinc (Zn) was removed up to 50%, the amount of lead (Pb) removed was more than 70%.

The performance of electrocoagulation process was increased due to the pre-treatment of wastewater by MO seed cake. The most optimally purified water was taken for electrocoagulation. The Fe-Fe electrode combination at pH 8 is observed to be more efficient for the treatment of electroplating industrial wastewater and the optimum time is observed to be 30 min. It has been noted that electrocoagulation process is capable of having high removal efficiency of COD, heavy metals, and sulphates. After electrocoagulation it was noticed from our results that more than 90% Chromium (Cr), Zinc (Zn) and Copper (Cu) were removed from water sample and the Cobalt(Co) and lead (Pb) was completely removed.

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