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Role of Titanium Oxide Nanoparticle on Heavy Metal Reduction in Electroplating Waste Water Treatment

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Abstract: Constructed wetlands are most biologically diverse and productive natural ecosystems involving wetland vegetation, soils and biological action to improve quality of waste water. These wetlands play a vital role in the removal of heavy metals such as Chromium, Cadmium and Lead and with the introduction of nanoparticles like Magnesium and Titanium dioxide; offers a great possibility of removal of effluents and heavy metals to a great extent. Nanoparticles in constructed wetlands give good result due to its high surface area and this can be used large scale water purification.
The aim of this study was to compare the efficiency of the wetland technique conventionally and with nanoparticles. In normal wetland unit, electroplating water and domestic water are mixed in ratio 1:2 due to high concentration of heavy metals and it was found that there is decrease in the concentration of heavy metals as an average 90 % in 5 day and when adsorbent (Cicerarentinum seed coat) is used to reduce the toxicity of Chromium so that plant species in wetland unit is not affected and it was found that reduction in Chromium concentration is about 90.85% in 2 day and is completely below the discharge limits, whereas when nanoparticles are introduced in wetland unit it has an efficiency of over 90-96% removal of Chromium, Cadmium and Lead impurities from the polluted water with Titanium dioxide being the best and most efficient in the removal of these impurities.
Keywords: Constructed wetland, Nanoparticles, Magnesium, Titanium dioxide.

1. Introduction

Electroplating involves the deposition of a thin protective layer onto a prepared surface of metal using electrochemical processes. Any substances used in electroplating (Such as acidic solutions, toxic metals, solvents and cyanides) can be found in the wastewater. The overall wastewater stream is extremely variable (1 litre to 500 litres per square meter of surface plated) but usually high in heavy metals (Including Cd, Cr, Pb, Cu, Zn and Ni), Cyanides, fluorides and oil and grease.

Nanotechnology and constructed wetland technique offers good solution for the treatment of industrial effluents. Nanotechnology is the engineering of extremely small particles at the molecular level to create materials with new behaviors and chemical properties. Nanoparticles are more reactive for geometrical reasons as the proportion of surface atoms increase as the size of the particle decreases. Surface atoms are strongly inclined to make use of their bonding possibilities[1].

The ability to see nano-sized materials has opened up a world of possibilities in a variety of industries and scientific endeavors. Nanotechnology is essentially a set of techniques that allow manipulation of properties at a very small scale. It has a very wide range of applications and can effectively be used as sensors to improve monitoring standards and detection capabilities offering better controls for more efficient use of materials. Nanotechnology can be used for treatment of waste streams for cleaning it from contaminants particularly those substances that are highly toxic, persistent within the environment and which are difficult to treat. This can also be used for remediation, cleanup of contaminated sites, green manufacturing and for production of green energy[2].

Wetlands are the land in which the water table is above or at the ground surface level for sufficient time to maintain saturated soil conditions and the growth of micro-organisms and related vegetation's. Treatment of wastewater using constructed wetlands technology is considered especially applicable to closed landfill cells with simple soil cover systems, and low landfill gas production rates [15-16]. Vertical flow technology has the ability to maintain high dissolved oxygen concentrations, high ammonia loading and heavy metals. This results in very high reductions of BOD and significant nitrification[3]. Volatile organics are removed by volatilization or biodegradation and ammonia can be released to the atmosphere directly or after transformation to the nitrogen gas in the nitrification and denitrification processes[4.] Constructed wetlands have been successfully applied for wastewater treatment in the USA and in European countries.

2.Experiment

The details of experimental work carried out is shown in Figure 1.

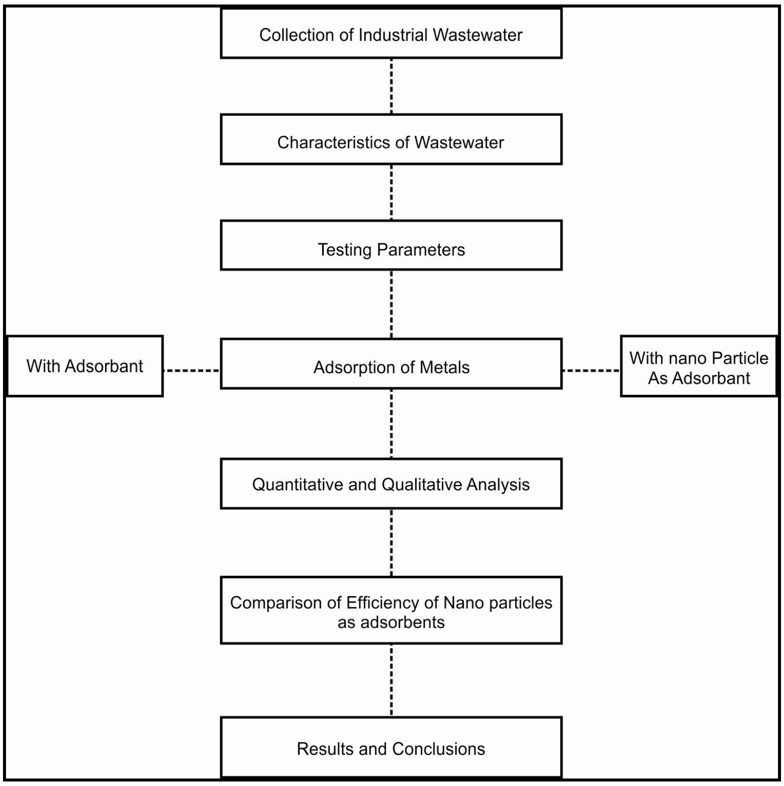

Figure 1 Flow chart of methodology

2.1 Analytical techniques

The wastewater characteristics were analysed using standard method as per APHA Manual and Heavy metal analysis was done by digestion and dilution of all the industrial effluents for analyzing concentrations of metals through Atomic Absorption Spectroscopy (AAS).

2.2 Preparation of samples

The samples were tested with lower concentration of industrial effluents. The samples were prepared at lower concentrations (4 concentrations of 30, 50, 70 and 100 ppm). Synthetic wastewaters as well as all the effluents were prepared at these concentrations and the amount of removal of heavy metals by different nanoparticles was analyzed by AAS[5].

2.3 Zero-Valent Iron nanoparticle

It was prepared by mixing equal volumes of 0.94M $NaBH_4$ and 0.18M $FeCl_3$. On stirring this at 400 rpm a black precipitate of Iron nanoparticles was harvested using vacuum filtration through 0.2 micron filter paper. The synthesized iron particles were washed several times with deionized water. Later the particles were sent for X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) analysis[6].

2.4 Magnetite nano-particle

It was prepared by mixing and stirring two equivalents of Ferrous Chloride Tetrahydrate with three equivalents of Ferric Chloride Hexahydrate at room Temperature. This mixture is treated by adding 100 ml of 28% ammonium hydroxide. Immediately the color of the solution changed from orange to black. Magnetite nanoparticles were harvested by magnetic decantation method[7].

2.5 Titanium Dioxide nanoparticle

These were synthesized using wet chemical technique. Vigorous stirring titanium chloride (2 ml) was drop-wise mixed in ammonium hydroxide or ethylene glycol and continuously stirred for 10 minutes. The reaction was exothermic and carried out in 100 ml beaker. This mixed precursor was heated to 333K (60^0 C). White particles were washed several times using warm water to remove chlorine impurities. Prepared particles showed amorphous phase. In order to convert it into crystalline phase, prepared particles were heated to 623K (350^0 C). After synthesis, the nanoparticles underwent full characterization[8].

2.6 Treatment of synthetic wastewater with nanoparticles

In case of all the three nanoparticles, the concentration of standard solution as well as effluents was taken in duplicates. To all the samples, 0.10 gram of adsorbent was added. After allowing it to stand for sometime all samples were centrifuged at 1000 rpm. After centrifugation they were filtered and filtrate was examined for metal concentration through AAS *11.*In case of Titanium dioxide, before centrifugation, suspensions were equilibrated in the dark for 10 minutes. Adsorption reactions were continued in the dark, while photochemical reactions were conducted under the illumination from a laminar flow equipped with Ultra Violet lamp. Later it was centrifuged[9].

2.7 Constructed Wetland

The primary criterion for design of inlet structure is discharge which should be uniform along the entire width in order to prevent short circuiting. A 20 liter container was used to provide a continuous flow of wastewater through the inlet. The pilot wetland unit was a PVC container of length, width and depth of 70 cm, 40 cm and 30 cm, respectively[10]. The unit was built with slight inclination of 1–2% between inlet and outlet zones. The media consisted of a gravel bed underlain by an impermeable layer. The bed was filled to a height of 7 cm with gravel of diameter 10–30 mm followed by a 7 cm thick top layer sand of 2 mm diameter. The top portion of the wetland unit was filled with local sandy clay loam soil to support vegetation.

Phragmites spp., a local wetland species, was used in the study. The plants were collected from a nearby lake and planted in the wetland unit. They increase the residence time of water by reducing velocity, and increase sedimentation of the suspended particles[11]. They also add oxygen and provide a physical site for microbial bioremediation. The plants have been used to remove suspended solids, nutrients, heavy metals, toxic organic compounds and bacteria. Outlet zone was designed to allow variations in the level of water discharge.

3. Results and Discussions

This study involves the percentage removal of Chromium and Lead by Zero Valent nanoparticles and constructed wetland technique using adsorbent and comparing the reduction of two process mechanism. The experimental values slightly deviate from the general values as the general values are the average values of research output.

3.1 Percentage removal of Chromium (Cr) and Lead (Pb) by nanoparticles

The samples were diluted to a range of 30 ppm to 100 ppm for Pb as well as Cr. Four Dilution concentrations of 30, 50, 70 and 100 ppm were analyzed. Two samples of each concentration were taken to get an accurate result. Then 0.1g of nanoparticles was added for treatment of metals in all the diluted effluents and synthetic wastewater. All the samples were analyzed by AAS after treatment. Percentage removal of Chromium and lead by Zero Valent Iron,Fe_3O_4Nanoparticle and TiO_2 Nanoparticle are discussed in Tables 1,2 and 3 respectively.

Table 1 Percentage removal of Chromium & Lead by Zero Valent Iron Nanoparticle

Name	Sample No.	Concentration of Pb before treatment in (ppm)	Concentration of Lead after treatment in (ppm)	Concentration of Cr before Treatment (ppm)	Concentration of Cr after Treatment (ppm)	% Removal of Cr	% Removal of Pb
Standard Solution	1	30	3.249	30	6.143	88.77%	79.55%
	2	30	3.487	30	6.125		
	3	50	18.687	50	14.023	62.37%	71.97%
	4	50	18.942	50	14.003		
	5	70	26.031	70	28.338	62.8%	59.6%
	6	70	26.045	70	28.216		
	7	100	55.453	100	50.268	43.10%	49.79%
	8	100	58.341	100	50.142		
Electro-Plating Industry	17	30	10.490	30	8.687	63.78%	70.63%
	18	30	11.246	30	8.938		
	19	50	21.978	50	19.263	53.17%	60.89%
	20	50	24.86	50	19.841		
	21	70	37.99	70	31.482	45.26%	56.05%
	22	70	38.642	70	30.048		
	23	100	58.903	100	48.942	41.08%	51.18%
	24	100	58.963	100	48.697		

Table 2 Percentage removal of Chromium & Lead by Fe_3O_4 Nanoparticle

Name	Sample No.	Concentration of Pb before treatment in (ppm)	Concentration of Lead after treatment in (ppm)	Concentration of Cr before Treatment (ppm)	Concentration of Cr after Treatment (ppm)	% Removal of Cr	% Removal of Pb
Standard Solution	1	30	0.124	30	0.00	99.59%	100%
	2	30	0.121	30	0.00		
	3	50	1.892	50	0.00	96.15%	100%
	4	50	1.962	50	0.00		
	5	70	5.238	70	1.375	92.59%	98.03%
	6	70	5.135	70	1.381		
	7	100	9.826	100	6.289	90.19%	93.69%
	8	100	9.782	100	6.324		
Electro-Plating Industry	17	30	0.109	30	0.00	99.64%	100%
	18	30	0.105	30	0.00		
	19	50	0.992	50	1.312	98.02%	97.37%
	20	50	0.989	50	1.322		
	21	70	1.216	70	2.942	98.27%	95.77%
	22	70	1.205	70	2.972		
	23	100	4.259	100	4.645	95.74%	95.28%
	24	100	4.165	100	4.797		

Table 3 Percentage removal of Chromium & Lead by TiO_2 Nanoparticle

Name	Sample No.	Concentration of Pb before treatment in (ppm)	Concentration of Lead after treatment in (ppm)	Concentration of Cr before Treatment (ppm)	Concentration of Cr after Treatment (ppm)	% Removal of Cr	% Removal of Pb
Standard Solution	1	30	0.110	30	0.00	99.62%	100%
	2	30	0.114	30	0.00		
	3	50	0.687	50	0.00	98.90%	100%
	4	50	0.742	50	0.00		
	5	70	1.236	70	1.375	98.03%	98.02%
	6	70	1.543	70	1.381		
	7	100	2.483	100	2.289	97.69%	97.65%
	8	100	2.216	100	2.324		
Electro-Plating Industry	17	30	0.109	30	0.00	100%	100%
	18	30	0.105	30	0.00		
	19	50	0.326	50	0.00	100%	100%
	20	50	0.321	50	0.00		
	21	70	1.265	70	1.758	96.70%	98.19%
	22	70	1.259	70	1.797		
	23	100	4.245	100	3.284	96.63%	96.81%
	24	100	4.135	100	3.448		

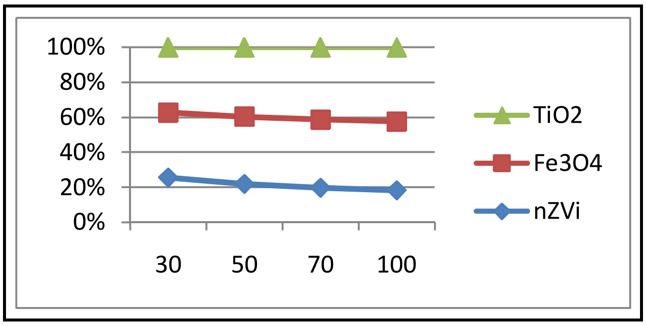

Figure 2 Percentage removal of Chromium by the three nanoparticles

The reduction percentage of chromium and lead by the action nanoparticles are discussed in Tables 1, 2 and 3. The comparison between the three nanoparticles for the common effluent is provided in Figure 2 and Figure 3. On comparing the values of Percentage removal of Chromium from the tables, obtained from the analysis of samples in the lab we found out that for Lower concentrations (between 30-100 ppm) Titanium dioxide has the highest percentage removal. At 30-ppm concentration, all the TiO_2 and Fe_30_4 nanoparticles were able to remove Cr with 100% efficiency. Values of nZVI and Magnetite reduced with increase in concentration. At 100 ppm concentration, nZVI caused 42.25% removal and Fe_3O_4 caused 90% removal while, TiO_2 caused almost 95% removal. The comparison of pH, TDS, Cr and Pb with respect to time is shown in Figures 4, 5, 6, and 7. Since Lower concentrations were used, the results were similar for Synthetic Wastewater, Tannery and Electroplating Effluents.

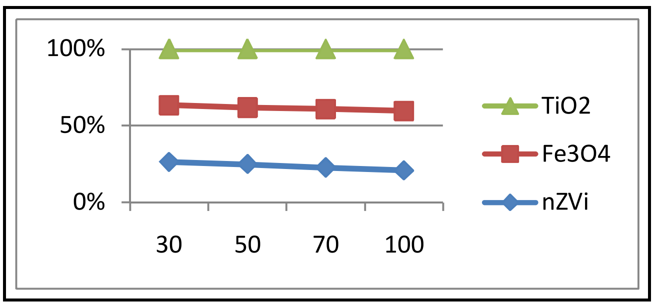

Figure3 Percentage removal of lead by the three nanoparticles

3.2 Wetland with adsorbent (Cicerarentinum seed coat) for Chromium and Lead

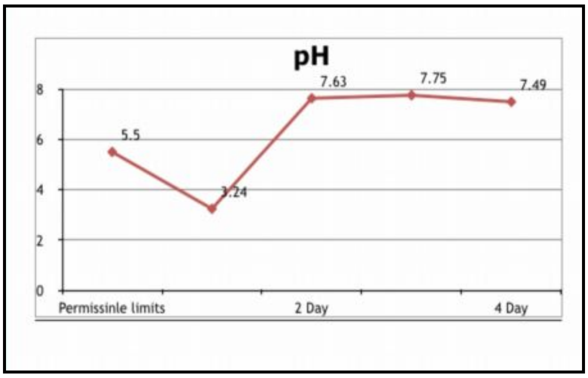

Figure 4 Comparison of pH

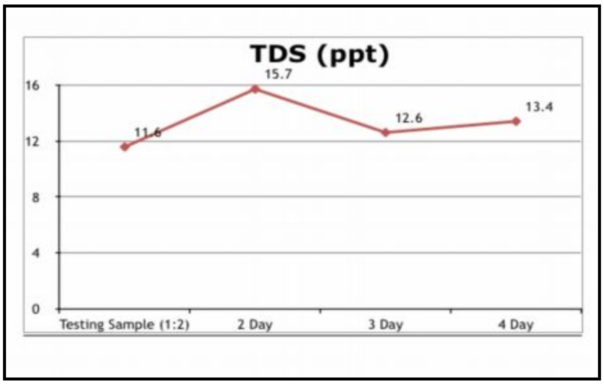

Figure 5 Comparison of TDS

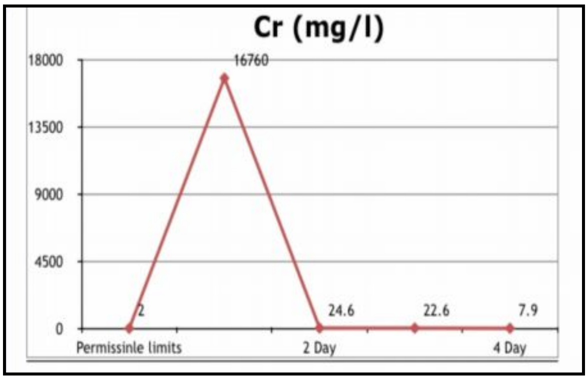

Figure 6 Comparison of removal of Cr

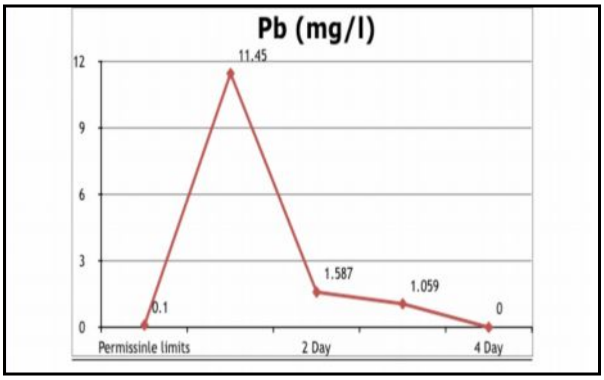

Figure 7 Comparison of removal of Pb

From the analysis it was clear that mainly hard chrome plating is done in this process shop. The result also reveals that there is stockpiling of the industrial effluent due to which the concentration of certain heavy metals was many times more than the usual discharge limits. As the concentration of heavy metal is too high, it is advisable to dilute the industrial effluent along with the domestic wastewater. The dilution ratio derived based on the pot culture study was 1:2 (one part electroplating water and two parts sewage waste) and this it was used for irrigation in the constructed wetland. There is remarkable decrease in the concentration of heavy metals as an average 98 % on the 6^{th} day when Cicerarentinum was used as adsorbent.

4. Conclusion

It is evident from the study that the Procedure opted here for synthesis of nanoparticles was simple and cheap as they were homemade recipes [12]. In Case of ZVI, it is a good adsorbent having good capacity to treat different kinds of waste. The major drawback is that it is prone towards oxidation, which would lead to incorrect results.

In case of magnetite nanoparticles, it is possible to reuse particles for 5-7 times. It is a good adsorbent but it has a less life because it is made up of Iron[13]. On the other hand TiO_2 needed UV source for irradiation but it shows very high efficiency in the treatment of heavy metals and there is no harm from the product during treatment. Since it does not contain Fe, it has no risk of oxidation. So, from all the three particles, TiO_2 is found to be most efficient in the removal of heavy metals from the effluents, as it has an efficiency of over 96% removal of Cr and Pb impurities from the polluted water.

In the mean time Constructed wetlands also working effectively in the treatment of electroplating wastewater treatment and for removal of heavy metal by the role of adsorbent and based on the analysis it was found that the treatment efficiency of 96 to 98% can be achieved with a retention time of six days[14]. If both techniques are combined and used for the treatment of industrial wastewater treatment it will give better efficiency with less retention time.

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