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Assessment of Tendu Leaf Refuses for the Heavy Metal Removal from Electroplating Effluent

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The tendu (*Diospyros melanoxylon*) leaves as refuse from bidi industry, contaminate the environment by its disposal and its degradation period is so long compared to other leaves. Adsorption process is carried out in shake flask condition using carbonized tendu leaf refuse as a adsorbent. The results obtained by the process of biosorption using tendu leaf for synthetic effluent show that the maximum efficiency achieved is 99.5% for chromium and 95% for copper at pH 5. In relation to electroplating effluent, the removal efficiency of chromium is 97%, copper is 96%, cadmium 81% and magnesium 75%. From electroplating effluent contaminated soil, the leachate was collected. 100% removal efficiency of all metals is noted. The isothermal studies showed good result for pH 5 and pH 7. The Langmuir isotherm fits to the data of the present study better than the Freundlich isotherms. Also the exprimental data follows pseudo-first order reaction.

Keywords: Biosorption, Electroplating Effluent, *Diospyros melanoxylon*, Isothermal Studies, Carbonized Tendu Leaf Refuse.

Heavy metals, the source of pollution in the environment impart serious crisis since these metals are non biodegradable and can accumulate in living organism. In electroplating industry the usage of different heavy metals leads to problem in environment because of their toxicity. Contamination of metals is a unrelenting problem in various contaminated sites. These metals in soil or in groundwater pretense major hazard to living organism and ecological systems. Heavy metal pollutants have its own varieties which sway their solubility, mobility, and toxicity in ground water in the form of leachate. Heavy metals can be emitted into the environment by both natural and anthropogenic causes. The main anthropogenic sources are mining operations. In some cases, even a long period after mining activities have ceased, the emitted metals continue to persist in the environment. Heavy metals are emitted both in elemental and compound (organic and inorganic) forms. The anthropogenic sources of emission are the various industrial points including the former and present mining sites, foundries and smelters, combustion by-products and traffics). Cadmium is released as a by-product of zinc (and occasionally lead) refining; lead is emitted during its mining and smelting activities, from automobile exhausts (by combustion of petroleum fuels treated with tetraethyl lead antiknock) and from old lead paints; mercury is emitted by the degassing of the earth's crust. Generally, metals are emitted during mining and processing activities[5].

The processes of attachment of atoms are ions to a surface are known as adsorption. Through adsorption, a film is created on the surface of adsorbent. The negative process of adsorption is desorption and both desorption and adsorptions are generally termed as sorption. Most widespread

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mechanism of bioremediation is biosorption[4]. In this process dead cells are used as a biological agent for remediating metal contaminants. Though living cells are more efficient in remediation process, due to their ability to multiply on their own and degrade metals effectively through different mechanisms[6]. They are more sensitive to various environmental stipulations and they requires proper nutrition as a energy source.

The dwelling industry of bidi making in India, makes wounding of tendu (*Diospyros melanoxylon*) leaves as refuse which contaminate the dumping sites[11] and produce solid waste disposal crisis. tendu leaf waste from bidi industry which is chemically treated to get activated biomass and it is examined for its efficiency in removal of the hexavalent chromium from aqueous solution. Tendu waste is characterized by scanning electron microscopy, porosimetry and BET surface analyses and other physico-chemical methods. For increasing the adsorption capacity, the tendu leaf waste is treated with glutaraldehyde, so that the waste gets activated by chemical treatment[10]. This research work focus on showing the reduction of metal in synthetic and electroplating effluent using biosorbent material such as Tendu leaves refuse. In this research, batch reactor studies were carried out to optimize the parameters such as contact time, pH, Temperature, and adsorbent dose. The experimental data analysis was preformed and it matches with different isotherms like Langmuir, Freundlich and Temkin isotherms. This study also focuses on the activation of adsorbent usage during adsorption process. Such activation yields better efficiency in the removal of heavy metals from contaminated site.

MATERIALS AND METHOD

Synthetic Metal Effluent Preparation

The metal solutions were prepared by dissolving the salt in distilled water and taken as synthetic solution for the treatment using biosorption techniques. 3.735g of potassium chromate was dissolved in distilled water,1g of cadmium metal in a minimum volume of (1+1) HCL, 1g of copper metal in minimum volume of (1+1) HNO_3 and 1g of managanese metal in a minimum volume of (1+1) HNO_3 .It is diluted to 1 liter with the concentration of 1000mg/L stock solution.

Sample collection

The metal effluents were collected from the electroplating industry, Madurai. 25 liters of effluent were collected in clean plastic cans. The effluent was stored at 4ºC for further studies. The biosorbent Tendu Leaf (Diospyros melanoxylon) refuse shown in *Fig 1* is used for the present study was collected from bidi industries in Alangulam village located in Tirunelveli, Tamil Nadu.

Preparation of biosorbent

Tendu leaf were cut in to pieces, then rinsed with distilled water and dried in an oven at 120 °C to get a constant weight. The dried tendu leaf refuse (TLR) was powdered to 0.2 to 0.3 mm size and stored in desiccator for ready use. Chemically modified carbon from tendu leaf refuse, Carbonized Tendu Leaf Refuse (CTLR) was prepared by acid base treatment using concentrated sulfuric acid in the ratio of 5:3 and kept in air tight oven at 120°C – 130°C for 4 hours. The carbonized mass was washed with distilled water to remove the acid, soaked in 1% solution of sodium carbonate over night to remove the residual acid. It was further filtered and dried at 110°C till it gets a constant weight[7]. The material was pulverized and sieved through to obtain 0.125 mm particle size as shown in *Fig 2* below and was used for the present study as CTLR. For increasing the adsorption capacity, the tendu leaf waste is treated with glutaraldehyde, so that the waste gets activated by chemical treatment[10].

SEM Analysis

Scanning electron microscopy (SEM) is used to recognize the morphology, elemental composition and also the particle density of the metal contaminated soil. The analyses were carried out with the help of a computer controlled field emission. SEM can also determine the structure and morphology of the media used for treatment. SEM results suggest that the media, ie immobilized media or adsorbent which contains a large particle size distribution as well as particles of major size, indicating that the material is a heterogeneous powder and its composition[1].

Batch studies

1litre of the synthetic metal solution with varying concentration, (25 mg/L,50 mg/L & 75 mg/L) and with varying pH, (3, 5 & 7) were taken and the adsorbent dosage varied as 0.2g, 0.3g, 0.4g, 0.5g & 0.6g (2-6 g/L) were used for the study. 100ml of synthetic metal solution was taken in 250ml Erlenmeyer flasks; they were kept in rotary shaker and the contact time was varied as 60mins, 120mins, 180mins, 240mins & 300mins. Likewise, for electroplating effluent the same procedure was followed. Zumriye, 2005 performed a sequence of experiments in a batch system to evaluate the outcome of the system variables. i.e. initial pH, termperature and initial metal ion concentration. The experiments were conducted at 27±1°C in a thermostatically controlled shaker. The samples were withdrawn from the shaker at the predetermined time intervals and the solution was separated from the adsorbent by centrifugation at 5,000 rpm for 20 mins. The supernant was analyzed using Atomic Absorption Spectroscopy (AAS) to validate the effective removal of metal.

RESULTS AND DISCUSSION

Carbonized tendu leaf refuse

Various treatment was carried out using CTLR and different heavy metal removal of each treatment was analyzed. The optimium parameters from better removal eficiency obtained from trials were identified and those optimized parameters were used for treatment of electroplating effluent. The characteristics of CTLR are summerized in the *Table 1*. The parameters were optimized in batch studies such as concentration of dye, contact time, pH and adsorbent doses.The kinetics of the adsorption process using tendu leaf follows the pseudo second-order kinetics[12].

The scanning micrograph clearly reveals the surface texture and morphology of the tendu leaf refuse and CTLR. *Fig 3* shows the surface texture of CLTR before involved in the treatment of electroplating effluent contaminated soil. Also represents that biosorbent surface is irregular and have large macropores .The *fig 4* revealed that the particles of CTLR after loading they appeared to be non porous .It is clear from SEM pictures of CTLR show considerable number of holes and spots where the waste material in effluent can be trapped. So that the efficiency in metal removal increases. reported similar morphological character of contaminated soil.

Effect of adsorbent dose

The percentage removal of chromium, copper, cadmium and magnesium increases with increase in adsorbent dosage. This can be quantified due to increased adsorbent surface area and also accessibility of more adsorption sites. Also increase in dosage of adsorbent increases the pores availability for adsorption. The adsorbent particle increases and the metals are attached to their surface. The optimum adsorbent dosage for the removal of metal from synthetic metal solution is 0.5g/100ml. Once the dosage of adsorbent increases, the percentage removal of metals starts decreasing. Tendu leaf refuse and chemically carbonized tendu leaf refuse attained equlibrium within 2 hour for phenol concentration 10-25 mg/L and 1 hour for phenol concentration 20-200 mg/L respectively[9].

Effect of contact time

Contact time is one among the important parameters in deciding the efficiency of adsorbent in adsorption process. Metal removal efficiency increases with increase in contact time. Initial removal of metals occurs immediately once metals come into contact with the adsorbent and the easily available active sites are occupied by the metals. Also metals need time for finding out extra active sites for metal binding. From the above experimental data we infer that the adsorbent which

Table 1. Characteristics of carbonized Tendu leaf refuse

S.No	Parameters	Characteristics value
1	Moisture (%)	5.45
2	pH (5% solution)	6.75
3	Ash (%)	4.15
4	Matter soluble in water (%)	1.01
5	Matter soluble in acid (%)	3.6
6	Bulk density (g/ml)	0.475
7	Surface area (m^2/g)	205

Table 2. Percentage removal of metals using CTLR at pH 5 and adsorbent dosage 0.5 g/100ml

Heavy metals	% removal
Copper	96
Magnesium	75
Zinc	95
Lead	90
Chromium	97
Cadmium	81

Fig. 1. Tendu leaf

Fig. 2. Carbonized Tendu Leaf Refuse (CTLR)

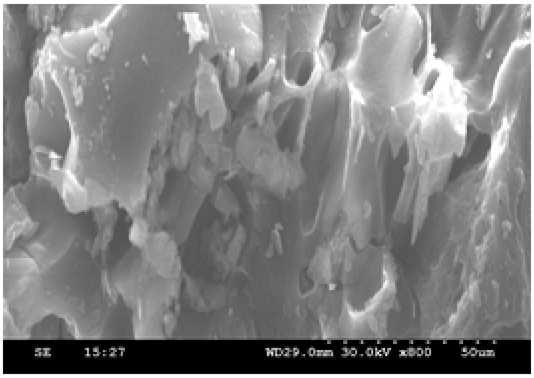

Fig. 3. CTLR before treatment with electroplating effluent

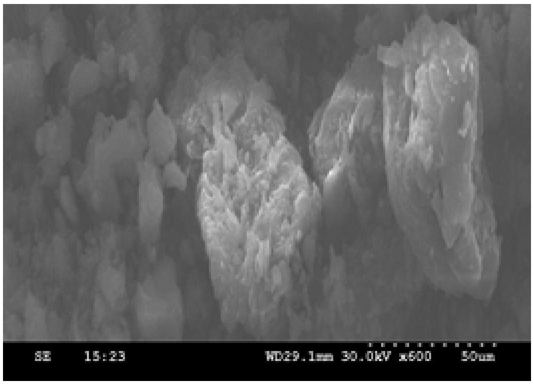

Fig. 4. CTLR after treatment with electroplating effluent

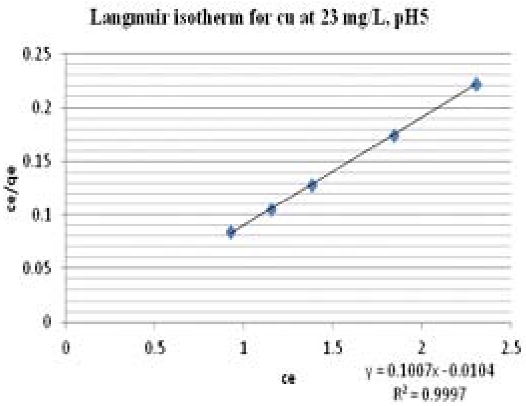

Fig. 5. Langmuir isotherm for copper

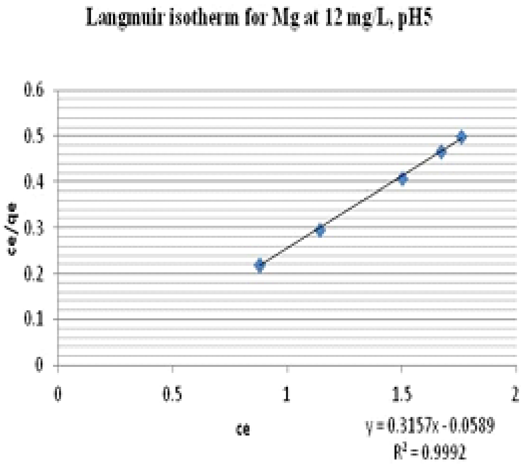

Fig. 6. Langmuir isotherm for magnesium

is in contact with synthetic metal solution for about 4 hours is more efficient in removing the metals and by attaining better removal efficiency. The efficiency of metal removal by activated tendu leaf at pH 2 increases more than 93% with increase in contact time, shows adsorption was consistent with time[7]. Surface sites during adorption turn into fatigued, the metal uptake rate is restricted by the adsorbent particle in the sites[14]. Initially adsorption efficiency is high and then gradually it drops down once the contact time increases. Thus if contact time increases, the concentration of the metal ion in the effluent does not shows any change[8]. The adsorption happens extremely quick primarily and reaches equilibrium within 60 min at pH 6.2 and the equilibrium attained quicker after altered with hydrogen peroxide[10].

Effect of particle size

Increase in metal removal efficiency increases with the decrease in particle size of the adsorbent; thus more surface area remains available for attachment of metal on the adsorbent surface. From this study, 0.125 mm particle size is found to be the best size to attain maximum metal removal efficiency.

Effect of pH

pH is also one of the important parameters significantly affecting the adsorption rate. Better metal removal efficiency was seen at pH 5 and pH 7. At low pH, adsorption of carbonized tendu leaf refuse get promoted and the active sites of adsorbent for binding of metals becomes less available, thus the metal removal efficiency decreases. If pH decreases the OH^- ions also decreases and if pH increases the OH^- ions also increases. So the pH maintained in the solution is between 5 and 9[3]. If the H^+ ions present in the solution is more it shows maximum adsorption even at low pH[2]. Once the pH increases the OH^- ions concentration also increases in the solution which results in declined sorption of chromium[3]. The metal removal is completely based on the pH of the effluent and the optimum pH obtained was 6.5 using Activated Teff Straw (ATS) as an adsorbent for removal of heavy metals like Cr, Cd, Pb, Ni, and Cu[8]. The adsorption of phenol declines by the raise of the pH value of the solution with tendu leaf refuse[9].

Adsorption isotherm

Isotherms are valuable in explaining adsorption capacity of adsorbent for evaluating the feasibility of the process, the choice of best adsorbent and for deciding the adsorbent dosage for treatment. The isothermal studies were performed for each concentration for the various parameters using the Freudlich and Langmuir

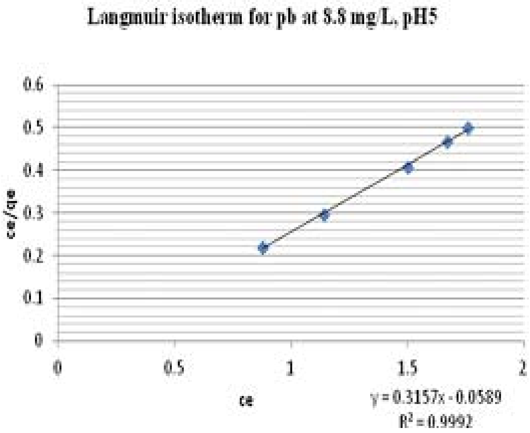

Fig. 7. Langmuir isotherm for lead

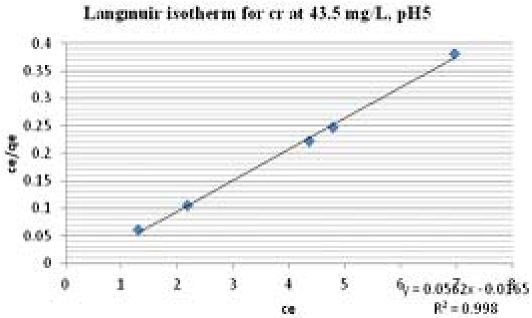

Fig. 8. Langmuir isotherm for chromium

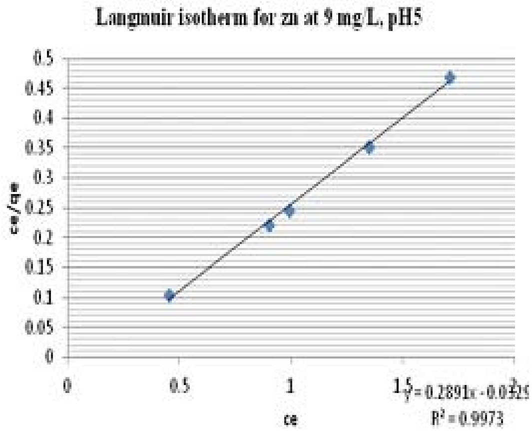

Fig. 9. Langmuir isotherm for zinc

model. These two models are commonly used for relating the adsorption equilibrium[7]. The result of heavy metals removal via adsorption were evaluated usind two models such as Langmuir and Freundlich isotherm[13]. It is important to evaluate the most suitable correlations for the equilibrium curves to optimize the design of an adsorption system. Equilibrium attained when the rate of adsorption of molecules onto the surface is the same as the rate of desorption of molecules from the surface. The results obtained are shown below for which the model is best suited and is favorable.

The results show that the biosorption capacity increases with increase in contact time and adsorbent dosage. Once it achieved optimum condition, the removal efficiency starts diminishing. The adsorbent dosage for the removal of various concentrations of metals from electroplating effluent was identified as 0.5 g/100ml as shown in the *table 2*. From the experimental data attained from the above studies is that, the optimum pH and adsorbent for the treatment of electroplating effluent is pH 5 and 0.5 g/100ml.

The equilibrium data obtained for carbonized tendu leaf refuse at pH 5, the adsorbent dosage varied in the range of 2 – 6 g/L. Both model shows monolayer biosorption but compared to Freundlich isotherm, Langmuir fits well with the experimental data shown in *fig 5 to 9* for all metals. Adsorption kinetics express the metal uptake rate and manage the residence time of adsorption process. It is also very important for identifying the efficiency of the adsorption process using CTLR. The data follwed pseudo-first order reaction fitting well in Lagergren plot. For adsorption of phenol on tendu leaf refuse fits best in pseudo-second-order reaction kinetics[9].

CONCLUSION

All biomass have their own natural capacity to act as biosorbent. Tendu leaf is a refuse from bidi industry, which act as a biosorbent. When chemically modified, they serve as activated carbon and enhance the capacity of treatment. The results obtained by the process of biosorption using tendu leaf for synthetic effluent show that the maximum chromium removal efficiency achieved at pH 5. For cadmium and magnesium, adsorbent shows maximum efficiency at pH 7.

From electroplating effluent contaminated soil, the leachate was collected and the treatment of leachate with adsorbent exhibits 100% removal efficiency of all metals. The isothermal studies showed good result for pH 5 and pH 7. The Langmuir isotherm fits the data better than the Freundlich isotherms. CTLR used as a adsorbent for adsorption process shows better removal efficiency. This is because; the easily available tendu leaves waste is capable of producing activated carbon that helps in the effective removal of metals from wastewater also reduces the solid waste problem in the environment.

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