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NATURAL COAGULANTS: AN EASY WAY TO REMOVE HEAVY METALS FROM TANNERY EFFLUENTS

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ABSTRACT

The seeds of *Strychnos potatorum* and *Moringa oleifera* are a natural coagulant which shows promising bioflocculant activity. These seeds are used to purify the drinking water in rural South India. In this research, an attempt has been made to analyze the biosorption of heavy metals by *Strychnos potatorum* and *Moringa oleifera* seeds from the tannery effluent. Heavy metals were estimated by atomic absorption spectrophotometer. The toxicity level of the treated effluent was analysed by green gram germination bioassay. Shoot length and root length of the germinated seeds were measured and seedling vigour index were calculated. The heavy metal removal efficiency of the seeds of *Moringa* and *Stychnous* was higher there by making both the seeds a promising candidate for industrial effluent treatment. These agro based compound could replace the chemical coagulant and is an environmentally friendly approach to effluent treatment.

INTRODUCTION

The use of natural coagulants in the water treatment was focused as an alternative to the expensive chemical coagulants. Chemical coagulants such as alum, ferric chloride, calcium carbonate, polyaluminium chloride and polyethylene amine were used as common inorganic coagulants in the water treatment units. These methods include electrochemical precipitation, ultrafiltration, ion exchange and reverse osmosis. A major drawback with precipitation is sludge production (Shetie Gatew et al., 2013). The residual of alum and polyaluminium chloride may produce the Alzheimer's disease and some of the synthetic organic polymers cause the neurotoxic and carcinogenic effect (Ndabigengesere 1995). Therefore, an attempt was made to use agro based coagulants as an alternate for chemical flocculants. The agro products would be more favorable of their low cost, abundance, environment friendly and does not leave toxic residues. Moreover, cheap and illiterate labor could be employed while treating the toxic tannery effluent in large scale.

The use of natural material of plant origin to clarify turbid surface water is not a new idea. The use of herbal materials to reduce turbidity or muddiness in the water and to remove the harmful biological material that can lead to illness is an age-old concept (Joshua and Vasu,. 2013).

Plants such as *Moringa oleifera*, *Strychnos potatorum, Jatropa curcas*, *Hibiscus sabdariffa*, *Clidemia aungustifolia*, *Cactus opuntia, Phaseolus vulgaris, Prosopis juliflora, Ipomea dasyspermand Gum Arabic, Guar gumas* coagulants have been used for water purification. Among these *S. potatorum* (Loganiaceae) and *M. oleifera* (Moringaceae) have shown as promising coagulant in the clarification of turbid water (Tripathi et al., 1976; Sutherland et al., 1990; Folkard and Sutherland., 2002). By reviewing the literature, it was observed that *S. potatorum* and *M. oleifera* seeds have natural coagulation property as well as used as an adsorbent to remove the heavy metals from aqueous solution (Jayaram et al., 2009; Joseph et al., 2015) reported that *M. oleifera* seeds and leaves as adsorbents shows the high extraction efficiency of the metals like Na, Fe, and Zn. The seeds of *S. potatorum* contained galactan and galactomannan which reduced the Cr (VI) from aqueous solution (Muthuraman and Sasikala, 2015). The surface modified *S. potatorum* seeds show higher adsorption capacity towards the removal of cadmium ions from aqueous solution (Senthilkumar et al., 2012). Hong et al., (2017) reported that a seed of *M. oleifera* has proved to be very effective in the removal of heavy metal like Cu, Cd, Zn, Ni, Mn and Fe in domestic wastewater.

Biosorption is a technically efficient, commercially viable and eco- friendly technology and it can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated/physico-chemical pathways of uptake (Fourest and Roux., 1992). Agro waste contains large quantity of polysaccharides and proteins with many functional groups such as carboxyl, hydroxyl, sulphate, phosphate and amino groups, which can bind metal ions. The performance of a biosorbent depends on its surface characteristics, which can be changed by modification process (Abdulsalam et al., 2014). The seeds of *S. potatorum* extracts are anionic polyelectrolytes which destabilize the particles present in the water by interparticle bridging, whereas the *M. oleifera* seeds contain active coagulant protein called a dimeric protein that have been used for various water treatment. The efficacy of these seeds was not examined for the biosorption of metals from tanning effluent were not studied elaborately. So far, the natural coagulant was used in the treatment of dye effluents.

The usage of biomass for the removal of heavy metals from the tannery effluent has not been given adequate attention. The aim of the present study is to examine the biosorption efficiency of *S. potatorum* and *M. oleifera seeds* by treating with tannery effluent and to analyze the uptake of heavy metals by them.

MATERIALS AND METHODS

- Collection of tannery effluent at Leather Tanning Industry, Vaniyambadi, Tamil Nadu, India.
- Collection of seeds at local Siddha Medical Shop, Ambattur, Chennai, Tamil Nadu, India.

Preparation of samples

The seeds were ground and sieved using 0.05 mm sieve and used as an adsorbent for the removal of heavy metals from the tannery effluent.

Physico-chemical analysis of tannery effluent: Physicochemical parameters of raw tannery effluent such as pH, Total Dissolved Solids (TDS), Total Solids(TS), Total Suspended Solids (TSS), Total Hardness as $CaCO_3$ equ, Cl^-, SO_4^{2-}, Cr^{3-}, Mg, Fe, P, COD, BOD were estimated using standard methods.

Treatment of raw effluent using *S. potatorum* and *M. oleifera seeds* powder: The Jar test experiment for treating effluent using natural coagulants was done. It was carried out by adding 10 gm/L of the seed powder to 1 L of tannery effluent separately and water as control. This study consists of occasional mixing, slow mixing and sedimentation. The set up was maintained for 7d at room temperature. The suspensions were allowed to settle down and separated by centrifugation (5000 × g). The supernatant and pellets were collected separately for analysis for heavy metal by Atomic Absorption Spectrophotometer (AAS). The weight of the pellet collected was determined and tabulated (Fig. 1).

Heavy metal analysis: The concentration of heavy metals in the tannery effluent before and after treatment and also the seed powder was analyzed using AAS. All the samples were acid digested for AAS analysis. The Atomic absorption spectrophotometer was heated with cathode lamp, the air acetylene flame was ignited and the instrument was calibrated with different working standards. The metals namely Cr, Cd, Zn, Fe, and Mg were detected in AAS (Elico instrument model SL 243 double beam) using respective standards. The biosorption percentage was calculated.

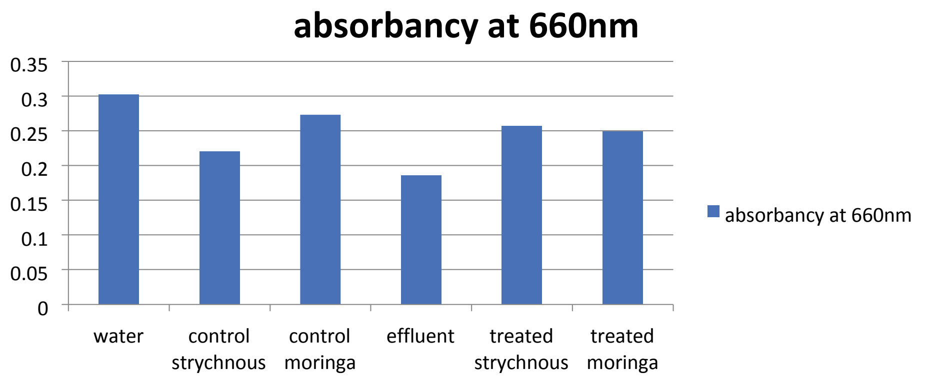

Fig 1. UV- Visible spectrophotometer analysis before and after treatment.

The percentage of removal and the metal ion sorbent amount onto the biosorbent was calculated as (Reddy et al., 2012):

Biosorption potential = $(C_o - C_e)/C_e \times 100$

Where C_o and C_e are concentration of the metal ion in the solution initially and after biosorption.

Bioassay: The germination of Vigna radiate seeds in treated tannery effluent was observed for 3 days and root length and shoot length were measured. Germination percentage and seedling vigour index was calculated as:

Germination% = $(n/N) \times 100$

N=No. of seeds introduced

n= No. of seeds germinated

Seedling Vigour Index = (Shoot length + Root length) × Germination%

RESULTS AND DISCUSSION

Physico - chemical analysis of tannery effluent

The physico-chemical parameters of tannery effluent such as pH (8.14), Total Dissolved Solids (10989 ppm), Total Suspended Solids (29 ppm), Cl^-(5680 ppm), Cr (8 ppm), Mg (349 ppm), COD (8569 ppm), BOD (3147 ppm) are presented in Table 1.

Effect of seed powder in the treatment of tannery effluent

Tannery effluent was treated with seed powder of *S. potatorum* and *M. oleifera* separately for 7 days. The treated effluent was separated by centrifugation at 2268 5000 × g. The pellets of treated seed powder and the treated effluent were estimated by AAS. The heavy metals namely Cr, Cd, Zn, Fe, and Mg were reported. From the Tables 2 and 3, it was found that the removal of heavy metal from the effluent was more by *S. potatorum* when compared with *M. oleifera. S. potatorum* seeds shows high biosorption potential of heavy metals in the order Cr >Cd>Mg>Fe>Zn and *M. oleifera* seeds in the order Cr>Zn>Fe>Mg >Cd. Biosorption of seed powder of both plants was represented in Table 4. Both the seeds biosorb Cr the most, whereas Zn was biosorbed least by *S. potatorum* while *M. oleifera* biosorbed the entire Zn ions from the effluent.

S. No.	Parameters	Experimental value
1	pH	8.14
2	Total Dissolved Solids	10989 ppm
3	Total Solids	11088 ppm
4	Total Suspended Solids	29 ppm
5	Chloride as Cl^-	5680 ppm
6	Sulphate as SO_4^{2-}	3148 ppm
7	Chromium as Cr^{3-}	8 ppm
8	Total Hardness as $CaCO_3$ equ.	2146 ppm
9	Calcium as Ca	324 ppm
10	Magnesium as Mg	349 ppm
11	Total Alkalinity as $CaCO_3$ equ.	518 ppm
12	Iron Content	0.05 ppm
13	Phosphate	Traces
14	Chemical Oxygen Demand	8569 ppm
15	Biological Oxygen Demand	3147 ppm

Table 1. Physico–chemical parameters of raw effluent.

S. No.	Samples	Chromium	Cadmium	Zinc	Iron	Magnesium
1	Control water	0.24 ± 0.058	0.23 ± 0.044	2.96 ± 0.159	7.15 ± 0.269	1.87 ± 0.221
2	Control plant	ND	0.50 ± 0.076	ND	1.18 ± 0.085	1.47 ± 0.139
3	Raw effluent	10.65 ± 0.336	1.97 ± 0.21	1.69 ± 0.284	10.16 ± 0.187	0.70 ± 0.036
4	Treated effluent	0.62 ± 0.072	0.55 ± 0.086	0.855 ± 0.092	4.61 ± 0.367	0.29 ± 0.155
5	Treated seeds	9.18 ± 0.099	1.40 ± 0.0717	0.685 ± 0.235	6.135 ± 0.648	1.22 ± 0.446
6	F value	3662	340.97	37.39	129.6	13.96
7	P value	0	0	0.0001	0.0001	0.0007

Table 2. Heavy metal analysis of treated effluent and treated *Strychnos potatorum* seeds.

S. No.	Samples	Chromium	Cadmium	Zinc	Iron	Magnesium
1	Control water	0.21 ± 0.176	0.21 ± 0.148	0.13 ± 0.053	6.03 ± 0.227	1.0 ± 0.078
2	Control plant	1.53 ± 0.112	0.44 ± 0.127	2.03 ± 0.028	8.67 ± 0.415	1.31 ± 0.113
3	Raw effluent	10.65 ± 0.336	1.97 ± 0.21	1.69 ± 0.284	10.16 ± 0.187	0.70 ± 0.036
4	Treated effluent	1.68 ± 0.091	1.87 ± 0.346	ND	4.82 ± 0.264	0.4 ± 0.108

5	Treated seeds	8.34 ± 0.376	1.11 ± 0.096	2.32 ± 0.218	7.9 ± 0.224	1.24 ± 0.159
6	F value	1160.26	22.7	405.24	746.18	119.99
7	P value	0	0.0001	0	0	0

Table 3. Heavy metal analysis of treated effluent and treated *Moringa oleifera* seeds.

S. No.	Samples	Chromium (%)	Cadmium (%)	Zinc (%)	Iron (%)	Magnesium (%)
1	Effluent+ *S.Potatorum*	94.17	72.08	49.7	54.62	58.57
2	Effluent + *M. oleifera*	84.22	5.07	100	52.55	42.85

Table 4. Biosorption % of Heavy metals by seeds.

S. No.	Sample	No. of Seeds	No. of Seeds Germinated	Germination %	Root length (cm)	Shoot Length(cm)	Seedling Vigour Index (VI)
1.	Control	30	30	100	8.8 ± 0.765	2.9 ± 0.519	1210
2.	Water with seeds	30	27	90	7.3 ± 0.643	2.4 ± 0.416	882
3.	Raw Effluent	30	12	40	1 ± 0.288	-	40
4.	Treated with seeds	30	18	60	3.3 ± 0.534	1 ± 0.165	258

Table 5. Effect of *S. potatorum* seed treated effluent on the germination of *Vigna radiata* and seedling vigour index.

S. No.	Sample	No. of Seeds	No. of Seeds Germinated	Germination %	Root length (cm)	Shoot Length(cm)	Seedling Vigour Index (VI)
1.	Control	30	30	100	8.8 ± 0.765	2.9 ± 0.519	1210
2.	Water with seeds	30	24	80	7.1 ± 0.504	2.3 ± 0.63	882
3.	Raw Effluent	30	12	40	1 ± 0.288	-	40
4.	Treated with seeds	30	18	60	3.3 ± 0.606	0.5 ± 0.2	228

Table 6. Effect of *M. oleifera* seed treated effluent on the germination of *Vigna radiata* and Seedling vigour index.

Bioassay

Bioassay is an analytical method to determine the residual toxicity level of the treated effluent using living cells or tissues. The toxicity of raw effluent and treated effluent was estimated by germinating Vigna radiate seeds. The shoot and root length were measured, germination percentage and seedling vigour index was calculated (Tables 5 and 6).

In this present investigation the powdered seeds of *S. potatorum* and *M. oleifera* were used to biosorb the heavy metals from the tannery effluent. This method was effective since the concentration of Cr, Cd, Zn, Fe and Mg reduced from the tannery effluent (Tables 2 and 3) and was biosorbed by the seed powder (Table 4). The *S. potatorum* seeds contain Strychnine a crystalline alkaloid which is responsible for coagulation properties (Radin et al., 2014)

M. oleifera contain cationic protein that can clarify turbid water. They are reactive in high pH (4-6) due to salting mechanism of protein. Seedling vigour index increased in treated effluent when compared to raw effluent. The raw effluent contains higher concentration of the heavy metals which is deterrent to the germination and after the treatment metal ion concentration reduced in the effluent which enhances the germination percentage and seedling vigour index of the seeds. The tannery effluent after treating with *S. potatorum* and *M. oleifera* could be used for watering the plants. Many researchers have reported on *S. potatorum* and *M. oleifera* seeds as ecofriendly and cheaper water purifier (Olsen 1987; Muthukumaran et al., 2013; Tripathi et al. 1976). Meneghel et al., 2013 stated that *M. oleifera* is biodegradable, non-toxic, non-corrosive and easy to use. *S. potatorum* was found to be environmentally friendly coagulants, which presented as a viable alternative for the treatment of wastewater and turbid water (Deshmukh et al., 2013). *M. oleifera* has potential as a natural Chromium removal agent that can be adopted by developing countries at low cost (Camilla, 2014).

CONCLUSION

This research finding on biosorption ability of seeds like *S. potatorum* and *M. oleifera* in the treatment of tannery effluent was more effective. The tannery effluent after treating with these seeds could be used for irrigation purpose after investigating if there is any bioaccumulation of heavy metals in crop plants. The seed powder after treatment could be burnt and the adsorbed metals could be re-extracted. These seeds are a promising candidate for industrial effluent treatment to make water treatment process easier and environment friendly and it could replace the chemical coagulant.

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