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Biosorption of Heavy metals and Dyes using Plant Weeds – A Review

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Abstract : Nature has derived populous biomaterials for the eradiaction of various pollutants from the environment. The plants are considered to be the prime source for biosorption of toxic metals and they are renewable sorbents. This process binds the hazardous metal ions from the aqueous solution on to the surface of the biomass. The biosorbents include agricultural wastes, few fungal, bacterial, plant biomass, animal biomass, enzymes, polysacchrides and industrial biowaste materials for remediation. This technique is environmental friendly clean up biotechnology and economical since the chemical oxygen demand of the waste water do not increase. The sorption of few heavy metals and dyes using the plant weeds like Eichhornia crassipes and Prosopis juliflora opended the way for alternate green technology. The biosorption of few heavy metals and dyes using the plant weeds are studied.This review helps to contribute intuitiveness for advanced research aimed at sagacious analysis of sorption methods and its applications.

Key words : Biosorption, toxic metals, dyes, adsorption, Eichhornia crassipes, Prosopis Juliflora.

Introduction

The biosorption process involves a solid phase called sorbent, a liquid phase called solvent and the dissolved species to be adsorbed called as sorbate present in it. The presence of functional groups like alcohols, ketones, aldehydes, phenols, carboxylic acids, ester groups and ionization of these, helps in cation binding[1, 2] properties during the biosorption process. The sorption process continues till the equilibrium is established between the solid bound sorbate species and its remaining in the solution[3].The waste water from the textile industry is found to contain complex inorganic, organic, hazardous dyes [4].The dye compounds are dark in colour and blocks the penetration of sunlight into the water and affecting the water ecosystem [5,6 ,7].The chemical oxygen demand, biological oxygen demand, total suspended solids, heavy metals are exceeding the permissible limit in the textile waste water. The increased load of metal like lead, chromium, cadmium and copper due to domestic and municipal discharges threatened the habitats of the plants[8]. The azo dyes are of most concern due to their hazardous effects in water leads to mutagenic, allergic, toxic, carcinogenic properties in aquatic organisms[9, 10] .In order to sequester these toxic metals, dyes and various pollutants several non-conventional low cost biosorbents, like wastes from agriculture and forestry[11] , several plant biomass, micro-organisms are used by various investigators and in this paper the two known invasive weeds Water hyacinth and Prosopis juliflora used as adsorbent by various investigators are reviewed.

Materials and Methods

Dye sorption method

The root of Eichhornia crasippes, REC, stem of Eichhornia crasippes, SEC, leaves of Eichhornia crasippes, LEC and entire of Eichhornia crasippes plant, EEC were oven-dried at 60°C and the particle size between 0.3 and 0.5 mm were used in the amaranth dye[10] biosorption experiments by the investigator. Total ash content was determined by using muffle furnace at 600°C. 120 mL of amaranth red dye solution at an initial concentration of 50 mg/L at pH of 2.0 ± 0.1 was mixed with 1 g of dry weight/L of biosorbent by the author. At ± 1°C for 48 hrs to achieve biosorption equilibrium, the author with the help of shaker agitated the flask at the speed of 120 rpm.

Results showed the rate followed pseudo-second-order $k_{2,}$ as shown in the Table 1. The biosorption capacity of amaranth dye q_e exp, using LEC-43.1 mg/g > EEC-31.18 mg/g > REC-28.5 mg/g > SEC-23.97 mg/g. At the equilibrium time $t_{e,}$ LEC-7 hr > EEC, REC-6 hr > SEM-4 hr. The author concludes that greater the values of q_e exp and t_e, the lower the value of k_2.Large amounts of the dyes is bisorbed when the time to reach the equilibrium state is longer.

Table1.Parameters of the pseudo-first-order, pseudo-second-order for amaranth dye biosorption [10]

Pseudo-first-order						**Pseudo-second-order**			
Biosorbent	**q_e exp (mg/g)**	**qe1 (mg/g)**	**k_1 (1/h)**	**r^2**	**RMSE**	**qe2 (mg/g)**	**k_2 (g/mg h)**	**r^2**	**RMSE**
LEC	43.096 ± 0.23	39.4 ± 0.84	1.036 ± 0.08	0.956	2.98	43.66 ± 0.69	0.032 ± 0.01	0.984	1.82
SEC	23.973 ± 0.29	22.68 ± 0.32	3.689 ± 0.28	0.931	1.99	24.04 ± 0.22	0.245 ± 0.02	0.977	1.15
REC	28.513 ± 0.59	26.51 ± 0.35	3.328 ± 0.23	0.945	2.16	28.38 ± 0.21	0.172 ± 0.01	0.986	1.08
EEC	31.181 ± 0.37	29.43 ± 0.45	2.562 ± 0.19	0.929	2.66	31.62 ± 0.37	0.119 ± 0.01	0.968	1.78

Biosorption of Heavy metal Chromium (Cr^{6+}) using Water hyacinth

The author prepared the adsorbent by drying it in sun for two days and also to avoid the degradation of binding sites dried in the oven for two hours at 70°C and then powdered sieved and used for batch studies to remove Chromium (VI) metal.200 mg of biomass powder was mixed with 50 ml of the metal ion solution of concentration5, 10, 15 and 20 ppm at pH 4.0 and after every 15 minutes the mixture was agitated and filtered. The removal increased from pH 2.0 to 4.0 and 81.21% was removed for 10 ppm solution. The percentage adsorption for different concentration shown in the Fig.1[12]

Biosorption of Lead ions[13] (Pb^{2+}) ions using Water hyacinth

The author prepared hyacinth compost and 1.2 g was added to Lead nitrate of 10 ppm and shaken for 60 minutes at speed of 150 rpm and the effect of pH performed at 2, 3, 4, 5, 6, and 7 was shown in Figure 2[13] .At optimum pH 5, Pb^{2+} ions was adsorbed and the author suggests that, due to the ionization constants of the carboxyl group adsorbents, the negative charge of the carboxyl group will bind to the positive charge of Pb (II).The maximum adsorption was 95.13%.The Freundlich isotherm models was studied by the author and the process of adsorption on the surface is heterogeneous in nature.

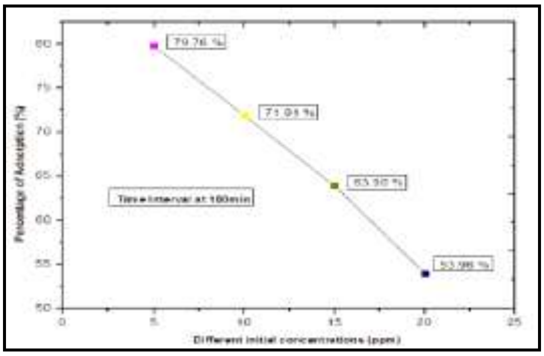

Fig 1.Cr(VI) ion adsorption at different concentration [12]

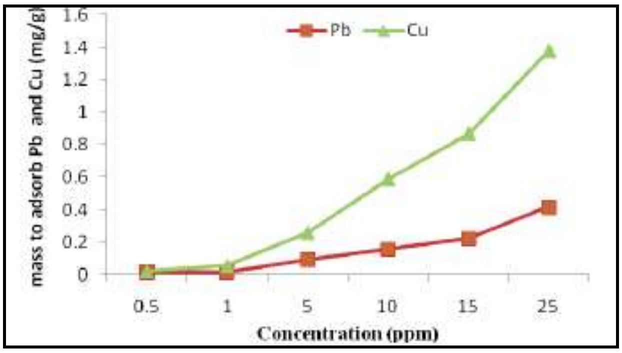

Fig.2.Determination of Optimum pH of Lead ions[13]

Biosorption of Lead ions[14] (Pb^{2+}) ions using Prosopis juliflora

The author prepared Prosopis juliflora seed powder by drying the plant in oven at 50 ° C for 2 days and sieved to give a fraction of 100 mesh screen. Using batch experiments 0.100g of adsorbent was added to the lead solution of concentration 20, 30, 40, 50, 60 mg/l at different pH. The adsorption increased to 85.1% in the pH range 2.0-6.0 at 28 ° C for 20 ppm of lead solution shown in the Fig 3. The pseudo-second-order kinetic model provided the best correlation, R2 = 0.9992 of the experimental data compared to the pseudo-first-order kinetic model.The adsorption isotherm follwed Langmuir equation

$$\frac{C_e}{q_e} = \frac{C_e}{X_m} + \frac{1}{q_m K_L}$$

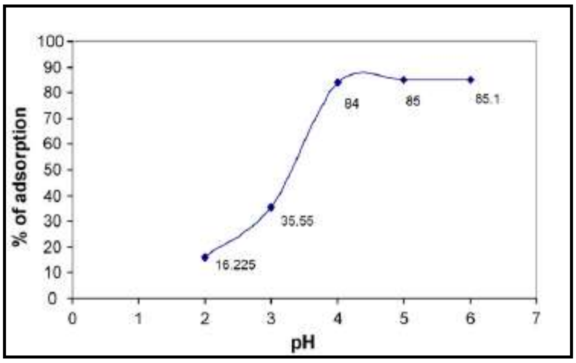

Fig 3. Effect of pH on lead ions [14]

Biosorption of Iron [15] (Fe^{2+}) metal ions using Prosopis juliflora

The powdered adsorbent was prepared by the investigator by drying it in the oven at 90-100 ^{0}C for 8-10 hours and the particle size was selected. The metal ions $Fe^{2+}$was prepared by dissolving FAS in the distilled water. The effect of contact time was studied at temperature 293K to 333K for the pH 2 to 7 by mixing 1g of adsorbent with the iron solution of concentration 1ppm to 4ppm.As the Temperature increased the number of adsorption sites also increased. The metal ion adsorbed also increased with the increase in pH shown in the Fig.4. Due to the effect of competition from H^+ ions decreases and the positive charged ions take their place on the surface. At low pH the H^+ ions are much larger than Fe^{2+} ions. 88% Fe (II) was removed from the adsorbent of 1g/100ml.The equilibrium adsorption data showed the adsorption followed second order kinetics. It is represented by the equation,

log x/m=log k+1/n log Ceq

Plotting log x/m vs. log Ceq a straight line was obtained with a slope of 1/n, and log k is the intercept. The k value was found to be 9.85.The value of ‘n’ was calculated to be 1.1784as shown in Fig.5.

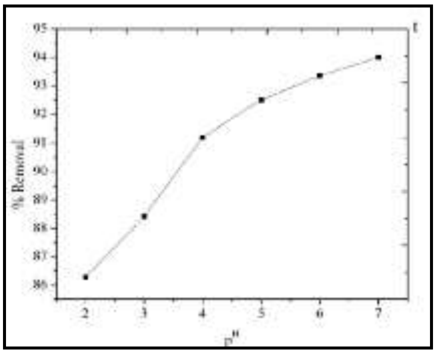

Fig4. Effect of pH[15]

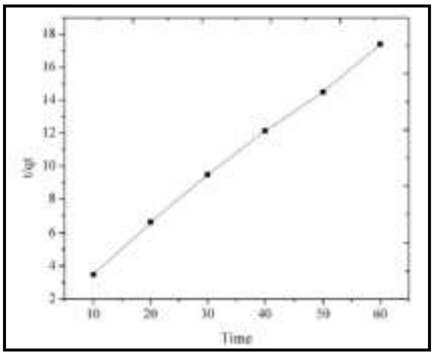

Fig.5 Effect of contact time[15]

Biosorption of Aniline Blue Dye[16] using -Prosopis juliflora Polymer beads

The investigator has prepared a polymer bead from the weed, Prosopis Juliflora by soaking the bark of the plant with H2 SO4 of ratio 1:1 for two days and washed till the pH was neutral. Then it was dried in oven at 120 ˚ C for two days and also carbonized in muffle furnace at 450 ˚ C. The author prepared particle size of 180–300 m by the sieve. Aniline Blue dye of formula $C_{32}H_{25}N_3Na_2O_9S_3$ was prepared by dissolving required amount and boiled to 80 ˚ C and 1.2 g of sodium alginate powder was added and stirred well for 45 min to get a clear solution. The author added to this 1.2 g of the adsorbent carbon and stirred for half an hour and calcium chloride was added in drops to get the polymeric bead after several washings. It was confirmed by the author using the Fourier Transform Infrared Spectroscopy. The adsorption was studied at pH range 3 to 10 for various concentration of dye from 10 to 70 mg L−1. The pH with a value of 6 shows a higher percentage removal and 60 mg L−1 of dye concentration shows 98.61% of removal at the contact time 60 min. adsorbent dose of 1 g shows 98.6%. As the Temperature increased the adsorption increased slowly and at room temperature it was 98.2% shown in the Fig 6.

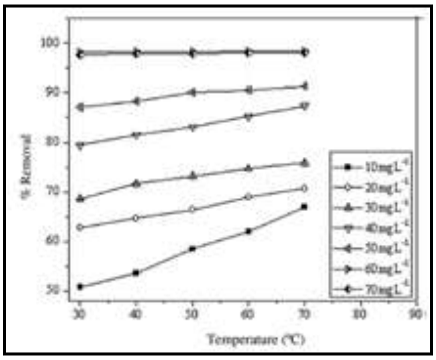

Fig 6. Effect of Temperature on the Adsorbent Poymer beads

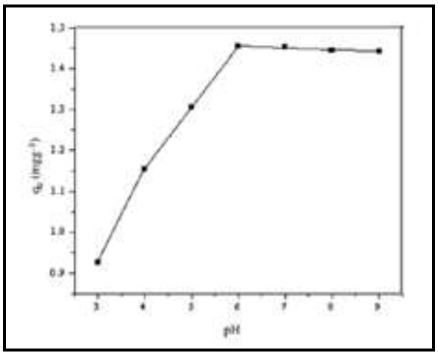

Fig 7.Effect of pH on the Adsorbent Beads[16]

Biofuel production from the weeds [17]

The investigator reported Bio-oil production from Prosopis juliflora fly ash at microwave power 560W for 50 g of fly ash of particle size 2 to 4mm shown in table 2.The author revealed the mixture of various fractions like Phenolic compounds, aromatic hydrocarbons, ketones, furan derivatives etc., shown in the Fig. 7. Below the temperature range 500 °C, 40% weight of bio-oil is obtained using 1/100th by mass of fly ash. This corresponds to 59% energy recovery along with 51% deoxygenating in bio-oil. Water hyacinth contains very high nitrogen content and when it is mixed with cow dung it produced more biogas than when used alone [18, 19.] The waste slurry is also used as biomanure and the bios mass is fermented to produce bio ethanol. The Bio ethanol production from the byproducts of Photosynthesis and fermentation using microbes like Escherichia coli is given below [20].The composition of water hyacinth and land plants are shown in the Table 3.

$6CO_2 + 6H_2O + \text{solar energy} \rightarrow C_6H_{12}O_6 + 6O_2$

$C_6H_{12}O_6 \rightarrow 2C_6H_5OH + 2CO_2 + \text{Energy}$

(Glucose) (Bio-ethanol)

Table 2. Percentage of oil yield for the partilce size 2to 4[17]

Susceptor	**Prosopis juliflora fly ash ratio (wt/wt)**	**Microwave power (W)**	**Particle size (mm)**	**Temperature (^{0}C min $^{-1}$)**	**Oil yield (wt %)**
Flyash	100:1	280	2-4	19.31	29.84
Flyash	100:1	420	2-4	38.24	35.41
Flyash	100:1	560	2-4	52.56	36.74
Flyash	100:1	700	2-4	76.00	36.64
Flyash	5:1	560	2-4	60.75	34.55
Flyash	400:1	560	2-4	73.23	38.66
Flyash	1000:1	560	2-4	65.33	34.48

Table.3. Composition of Water hyacinth and Land Plants[19, 21]

Components	% Composition in Water hyacinth	% Composition from land plants
Ligin	10	15-30
Cellulose	25	30-50
Hemicellulose	35	20-40
Ash	20	-
Nitrogen	03	-

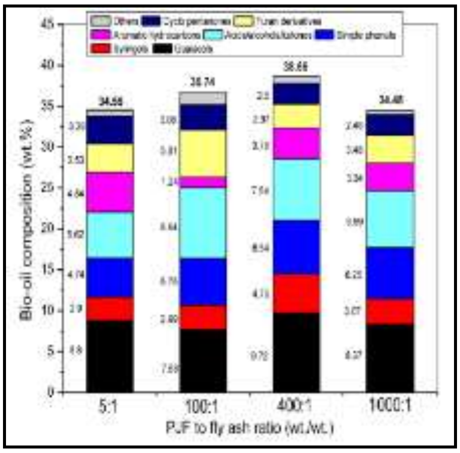

Fig.8.Bio- oil composition at different Prosopis juliflora fly ash ratio

Eichhornia crassipes

The aquatic weed water hyacinth shows biomass over 60 kg/m^2 [22] also it exhibits anti bacterial, anticancer[23], antifungal[24], anti inflammatory[25], anti oxidant properties[26 , 27]. The evaporation rate from the water bodies is ten times more in the presence of water hyacinth, also it blocks the breeding ground of the fishes [28] affecting the navigation, boating, agriculture and municipal water supply[29, 30]. 3,4,5-trihydroxycyclohex-1-ene-1-carboxylic acid, called shikimic acid[26] shown in the fig.9, is rich in water hyacinth and it is an intermediate in the biosynthesis of aromatic amino acids like phenylalanine, tyrosine and tryptophan[31] .It is commercially called Tamiflu, shown in fig.10, is an oral antiviral to treat influenza viruses[32,33]. Water hyacinth was shown to be an abundant source of useful antibiotics active against some pathogenic strains of bacteria, fungi and algae[24] and antioxidant properties against cancer cells[34]. The author reveals dry matter content in water hyacinth varies from 8.7 to 9.3 g/100g, crude protein content varies from 10.1 to 11.2 g/100g, Crude fibre content from 26.1 to 27.4 g/100g, Nitrogen free content varies from 47.2 to 50.2 g/100g and ash varies from 12.3 to 12.4 g/100g [35]. Water hyacinth shown in fig.14, have nematicidal property and hence can be used in the control of root knot nematode – Meloidogyne incognita [36] tolerates a temperature range [37] of 21.1 to 27.2^{0}C and used as paper, fuel, compost, animal feed, folkoric medicine[38] and as adsorbent for purifying water .The extract was found to contain some alkaloids[23, 24], flavonoids[41], glycosides and phenolic compounds[39] .This plant is the worst aquatic weed since it reproduces sexually by its seeds[40]

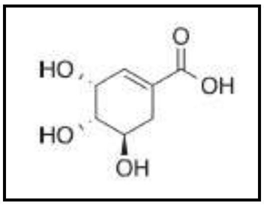

Fig. 9.Shikimic acid [26]

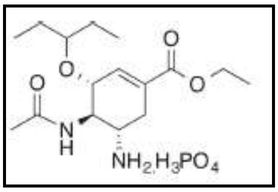

Fig.10. Structure of Oseltamivir phosphate or Tamiflu [26]

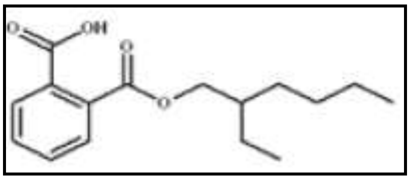

Fig.11: Alkaloid (1,2-Benzene dicarboxylic acid, mono-(2-ethylhexyl ester)[44]

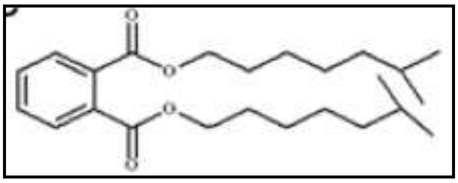

Fig.12:Terpenoid (1,2 Benzene dicarboxylic acid, diisooctyl ester) [44]

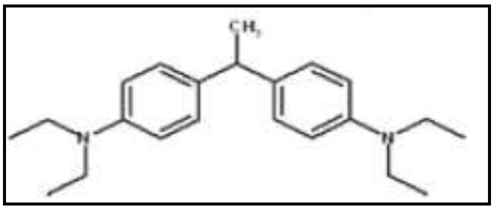

Fig. 13: Terpenoid (4-(diethylamino)-alpha-[4-(diethylamino)phenyl] [44]

Fig.14.Water hyacinth(Eichhornia crassipes)[35]

Fig. 15. Seemai Karuvelam (Prosopis juliflora)or algarroba [41]

Prosopis Juliflora

Prosopis Juliflora was brought to India in 1876 from the native Central America shown in fig.15. The plant was able to tolerate pH level of 9-10 and it was planted in arid tract of South India and Northern India. The antimicrobial activity[42, 43]was reported for the plant against 40 microbes and inhibitory effect was noted against Gram positive bacteria due to the presence of an alkaloid juliflоricine also antifungal, anti-inflammatory activities due to piperidine alkaloid[44, 45] shown in fig.16, 17and antialzheimer agent[46] shown in fig.18.Phytochemical analysis shows the plant contains alkaloids shown in fig.11, flavanoids, tannins, terpenes,terpenoids shown in fig.12,13 and few steroids [47].The plant is used as fodder for animals[48]

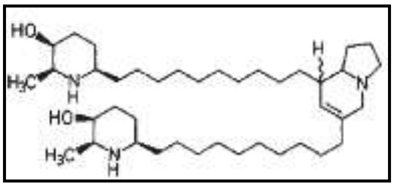

Fig. 16:Structure of Juliprosopin[49]

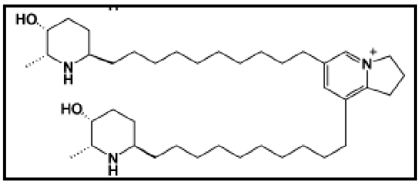

Fig. 17: Structure of Isojuliprosine[44]

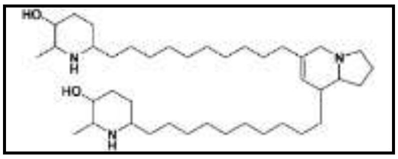

Fig. 18: Strucutre of Juliflorine[46]

Conclusion

Prosopis Juliflora and Eichhornia crassipes helps in the sorption of heavy metals and dyes. These weeds are harmful to the environment but also playing a vital role in the sequestration of hazardous metals and dyes from the water. These are found to be an alternative source for remediation. On the above studies done by various investigators these weeds are found to be a good adsorbent and environmental friendly. The alkaloid, flavonoids, tannins, terpenes and steroids present in these weeds plays a key role in binding the metal ions and the dyes from the water. These two weeds have found to have similar chemical and physical properties in sequestration process. The bio sorption technique helps the Environmentalist to find a slow and permanent solution for removing the hazardous compounds and it is the emerging Green Technology.

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