Kinetics and Adsorption Isotherm studies using Jatropha Curcas an Overview

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Abstract. Adsorption is one of the Physical methods employed to lower the concentration of pollutants. Presence of synthetic dyes containing azo group moeity, heavy metals like copper, cadmium, mercury, lead and chlorinated stain removers leaching from the dye industries are directly or indirectly mixing with the water bodies. They are considered to be a big challenge for the environmentalist to sequester these hazardous pollutants without adding chemicals further. Sequestration method using biosorbent are experimented by many scientist to remove the pollutants from the water bodies. An overview of biosorption of few dyes and metals using Jatropha curcas as adsorbent is studied. Adsorption follows Langmuir and Freundlich isotherm model. The Thermodynamic parameters such as ΔH^0, ΔG^0, ΔS^0 are reported. Jatropha curcas belonging to Euphorbiaceae family is gaining importance as good adsorbent.

Keywords. Biosorption, Adsorbent, Jatropha curcas, Thermodynamic parameters, Adsorption isotherm

1. Introduction

Biosorption is a method to sequester toxic heavy metals from the waste water using materials of biological origin[1]. This technology is found to have numerous advantages like high efficiency in detoxifying effluents, low operating cost[1-2] low volume of sludge disposal, no chemical requirements, environment friendly. The waste water effluent from the dye industry, textile industry, fabric finishing industry, paint industry are directly leaching into the nearby water bodies and polluting the ground water table. About 2, 80, 000 tonnes of textile dyes are annually discharged worldwide[5].These dyes contaminate the water and block the penetration of sunlight into the water and affect the photosynthesis process. This in turn affects the aquatic organisms and causes loss of habitat[4] and affects the food chain. Many dyes are found to contain azo groups which are resistant to fading when exposed to sunlight, water and they must be decolourised[6]. ·Years together many methods are followed by many investigators to neutralize the hazardous pollutants and new technologies are introduced for the same. Biosorption method is found to be one of the remedy to sequester the harmful dyes or metals, without harming the natural resources and further use of chemicals. Jatropha curcas is considered to be a good biosorbent to give bioremediation for the polluted water and soil. Many adsorption studies are done using the activated carbon of Jatropha curcas and this paper highlights the various sequestration techniques involved to biosorb the dyes and harmful metals from polluted sites.

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Jatropha curcas Origin

Jatropha curcas belongs to the family Euphorbiaceae. It is drought resistant, yields biodiesel and can be grown on marginal sites[3]**.**This tree is cultivated in Southeast Asia, India, Central and South America and Africa[7].The bark of the tree gives a dark blue dye and found to be rich in tannin[8].The leaves of the jatropha is also found to contain tannin which are phenolic compounds and posses antiinflammatory, antiviral, antifungal, anti-HIV, anticancer properties[34-36].

Pharmacological Properties of Jatropha Curcas

The extracts of Jatropha curcas is found to contain wound healing nature with less pain, tissue repairing and regeneration[9,10].The extracts is made into an ointment and applied for many dermatological purposes[11]. The latex of the tree is used against burns, ringworm, ulcers, heamorrhoids[12] the leaf extract to treat solid tumours[13] cytopathic effects of the human immunodeficiency virus[14].The seed is used as purgative, anthelmintic, also as a styptic[15] antidote for snake bites[16]used against eczema ringworm and scabies[17]. The tree possess pesticidal and insecticidal effects[18] used for domestic livestock against skin diseases, sores and piles[20].Few active compounds are shown in the Fig.1 and Fig.4.Solar cells dyed with jatropha curcas is found to have efficiency of 1.26% with open circuit voltage of 350mv[21].

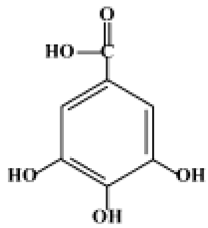

Fig.1 Structure of Gallic acid[33]

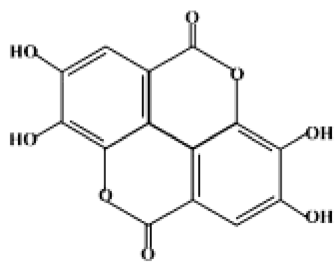

Fig.2 Structure of Ellagic acid[33]

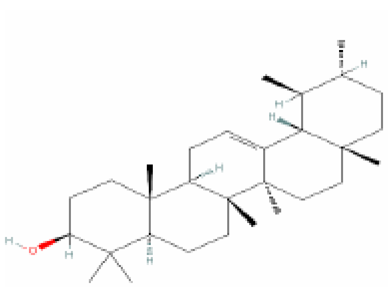

Fig.3 Structure of Alpha amyrin[20]

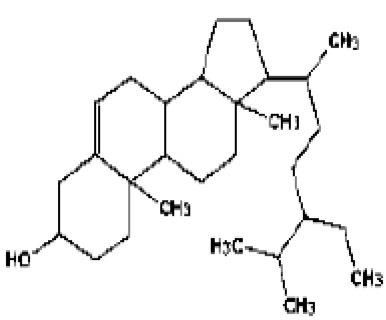

Fig.4 Structure of Beta sitosterol[20]

Dyes and Toxicity

Mauveine is the first synthetic dye produced by the chemist William Henry Perkinin in the year 1856.Dyes do not loose their colour when exposed to light, water, sweat or any chemical effects like oxidising agents and few microbial attacks[22].Most of the dyestuffs are azo compounds, mainly used by printing, textile, food, cosmetic and paper and pulp industries[23,24].

The azo dyes brings Intestinal cancer which is common in industrialized societies[25].Continuous exposure to Direct red 2 (azo dye) or its metabolites causes risk to health[26].The effluents rich in the dye contaminants affects the ground water and affects the people[27].The chromophore and the functional groups binds the dyestuff to the fiber[28]and the discharge of these non treated effluent affects the aquatic ecosystem and human beings[29]. Dye-containing effluents enter the water supply, possibly by contamination of the ground water; the general population may be exposed to the dyes via the oral route[27].

Adsorption Studies

Adsorption of Remazol Blue (Anthraquinone Dye) using Jatropha curcas

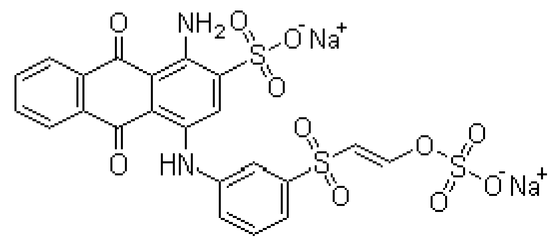

Fig.5 Remazol Brilliant Blue R[30]

The author prepared the adsorbent by purifying the plant and treating with con.H_2SO_4, and then the slurry was dried at 100 ^{0}C in hot air. The activated carbon was obtained by heating at 600 ^{0}C in oven. Various concentration of the dye shown in the Fig.5 was prepared and 0.1 to 0.5 g of the adsorbent was added and agitated at a speed of 160 rpm till equilibrium. The pH effects was studied by the author between pH 1 to pH 8 and maximum adsorption of 90% by 0.2 g of the carbon was found at pH 3.The adsorption isotherm shown in Fig.6 and Fig.7 indicates the separation factor, $R_{L=}$ 0.00087 and correlation coefficient (R^2= 0.979) confirms the adsorption is favourable. The Freundlich's adsorption isotherm[42] did not show linerization since R^2=0.64.

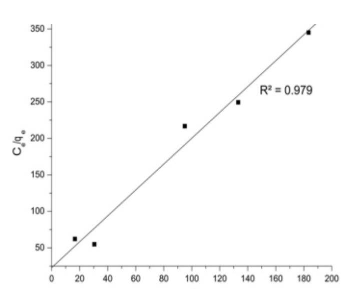

Fig.6 Langmuir isotherm of Remazol dye adsorption.

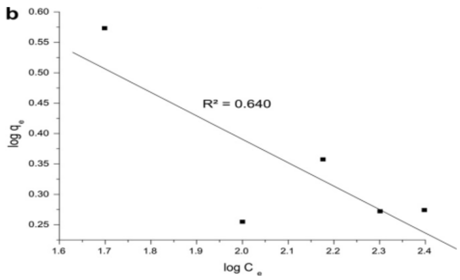

Fig.7 Freundlich isotherm of Remazol dye adsorption

Adsorption of Methylene Blue using Jatropha seed

Methylene Blue is a tricyclic phenothiazine drug shown in the Fig.8 used for treating malaria[31] Alzheimer's disease[32]

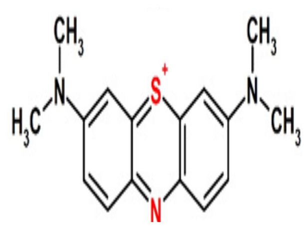

Fig.8 Methylene Blue[32]

The seed coats were thoroughly cleaned and charred at 500 ^{0}C. The particle size less than 90 µm was taken by the investigator for adsorption studies. Methylene Blue dye of different concentration was prepared and 0.02 g of the adsorbent was added to the dye and agitated at speed of 200rpm at temperature 28±2 ^{0}C. The pH increases from 2 to 4 and showed the adsorption of dyes indicated in Fig.9.

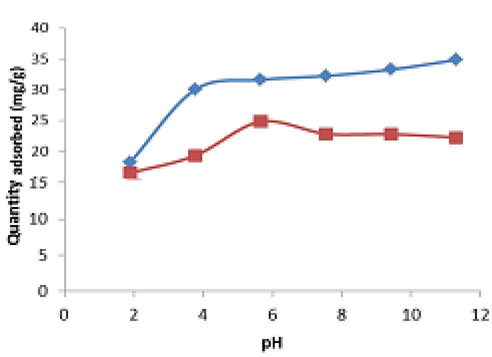

Fig.9. Effect of pH of adsorption of methylene blue[37]

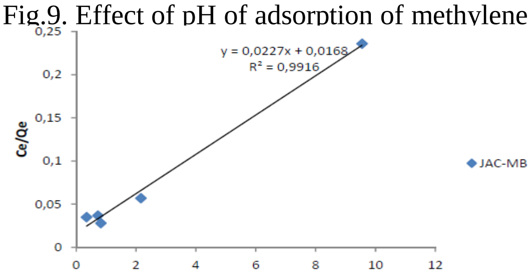

Fig.10 Langmuir plot of Methylene blue[37]

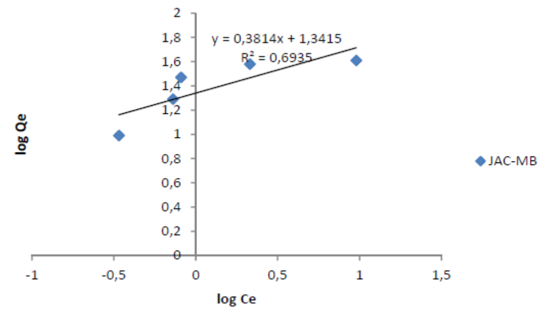

Fig.11 Freundlich plot of Methylene blue[37]

The Thermodynamic parameter shows ΔH is -12.68 KJmol^{-1}, ΔS is -24.06JK^{-1}mol^{-1}, ΔG is -4562 J/mol at 343K. The adsorption curve shown in the Fig.10, 11 fits into Pseudo second order kinetics model according to the author.

Adsorption of Acid Red Dye using Jatropha leaves

The investigator prepared adsorbent by purifying the Kattamanakku leaves with water, further dried in oven and soaked in sulphuric acid and heated in a muffle furnace at 100°C.Further dried in hot air oven at 333-343 K to get fine adsorbent powder of particle size 53-74 micro fractions. The adsorption was found to be maximum at pH 6.5 -7.5 as shown in Fig.12.At 300K the uptake of the dye was 52 to 63 %. The Freundlich adsorption coefficient, n, shown in Fig.13 remained in a narrow range of 0.51 - 0.66. The Freundlich adsorption capacity, K_f, was in the range of 2.42-9.47 Lg^{-1}. The Langmuir monolayer adsorption shown in Fig.14, C_1 was 4.26 and 11.32mg/g, separation factor R_L was 0.96.Since this value is close to 1.0 the adsorption curve was linear in nature.

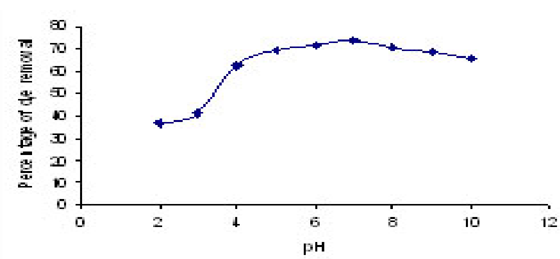

Fig.12.Effect of pH of Acid Red dye

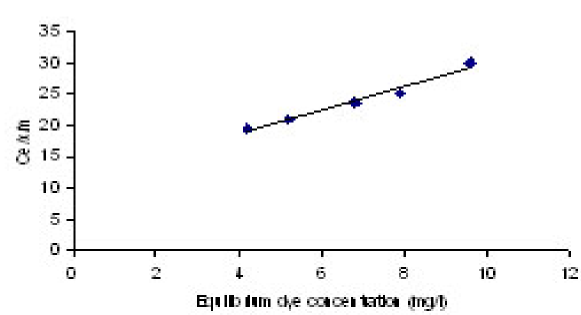

Fig.13. Langmuir isotherm for adsorption of Acid Red dye

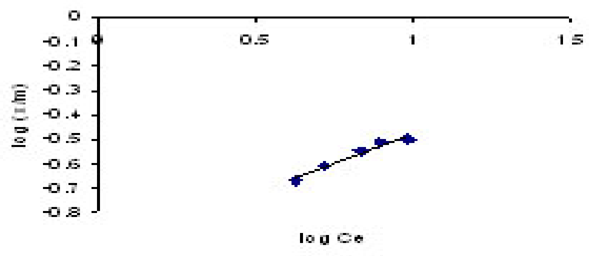

Fig.14 Freundlich isotherm for adsorption of Acid Red dye

Chemical Composition of Jatropha Curcas

Minerals/Pigments	Percentage %	Vitamins/Phenols	Percentage%
Nitrogen	1.99±0.007	B1(mg/g)	0.064±0.008
Phosporous	0.14±0.02	Niacin(mg/g)	0.049±0.006
Sodium	1.08±0.07	Flavonoids(mg/g)	0.540±0.011
Carotenoids(mg/g)	0.40±0.06	Tannins(mg/g)	0.870±0.16

Fig.15. Chemical composition of Jatropha Curcas [38]

Sorption of Metal copper ions using Jatropha seed coat

Jatropha seed coat was dried at 100 ^{0}C for 2 hours and sieved to 70mm mesh size by the author for adsorption of copper (II) ions. Copper sulphate solution was prepared by adding 2M nitric acid to avoid hydrolysis at different concentrations. 1g of adsorbent was added to 50 ml of the copper solution at 30^{0}C and rotated in a shaker at the spped of 125rpm. The effect of pH shown in Fig.16 of adsorbent increased with pH 4 to 6 and decreased beyond pH 5 due to copper hydroxide formation.When the adsorption equilibrium is reached the removal of copper ions was increased from 82% to 89% at concentration 20 ppm to 50ppm. The Langmuir adsorption isotherm Fig.17 shows the R_L value between 0 to 1at all concentration indicating good adsorption of copper ions. The Freundlich adsorption isotherm Fig.18 shows good correlation and "n" value was greater than one which implies sorption of new molecule occur with greater difficulty[39].

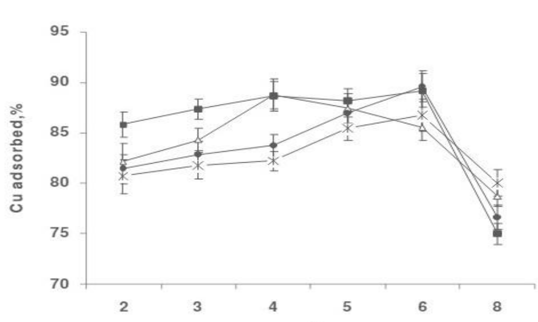

Fig.16. Effect of pH for adsorption of copper ions

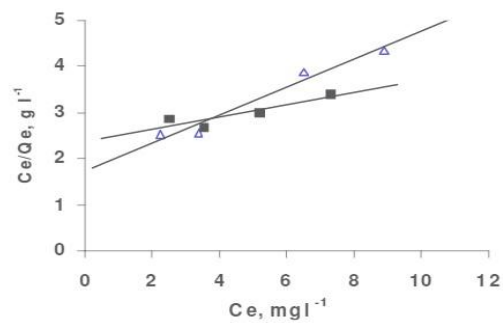

Fig.17 Langmuir isotherm for sorption of Copper ions

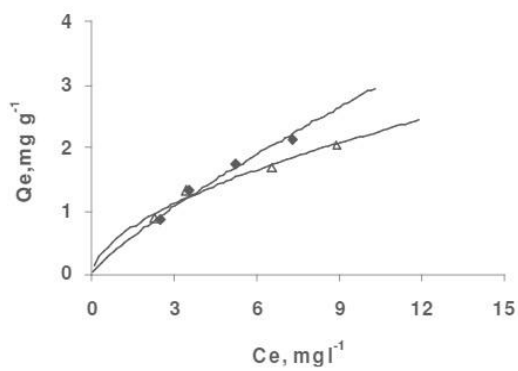

Fig.18 Freundlich isotherm for sorption of copper ions

Adsorption of Phenol using Zinc chloride activated Jatropha Husk

Jatropha husk was washed and dried in oven at 105±5 ^{0}C for 8 hour then crushed and mixed with zinc chloride and oven dried at 60 ^{0}C for 12 hours. Again dried to 800 ^{0}C in muffle furnace for 1 hour and cooled. The carbon so obtained was dipped in hot HCl solution for one day to remove zinc chloride.The next day it was placed in oven at 80 ^{0}C and dried for one hour. After removal of chlorides the material was oven dried and sieved to 250-500 microns by the author.100 mg of adsorbent carbon was mixed with 50 ml of phenol and agitated for 20 minutes at 2500 rpm. The effect of pH shown in Fig.19 for different concentration 20 ppm to 100 ppm was studied. At pH 11 the adsorption was less due to ionisation of phenol.The adsorption was 49 mg/g at pH 6.8. The adsroption kinetics followed second order and the Langmuir constants Q was 48.8mg/g and b was 0.16 L/mg according to the author.R_L value was between 0 to 1.Freundlich constant "n" was 2.02 shown in Fig.20 and thermodynamic constants ΔG= -24.69KJ/mole, ΔH= 1281KJ/mole and ΔS=84.34 J/K/mole[40].

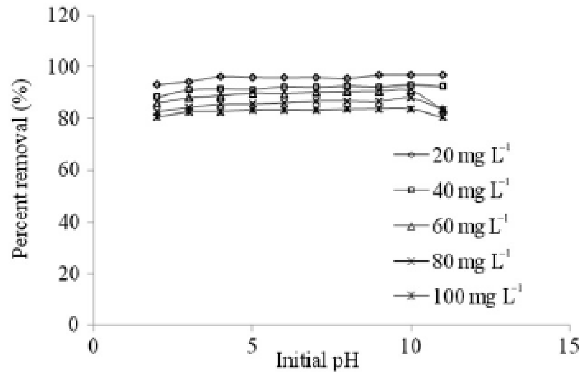

Fig.19 Effect of pH for adsorption of phenol

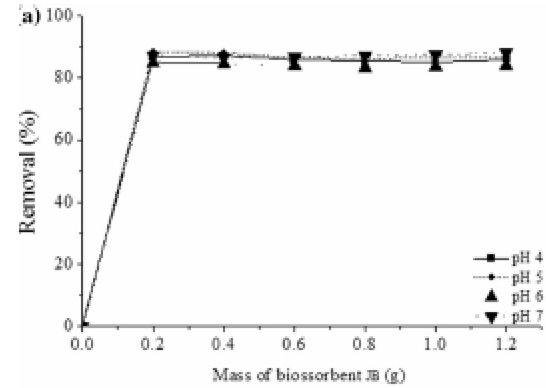

Fig.21. Effect of pH for adsorption of Cadmium ions

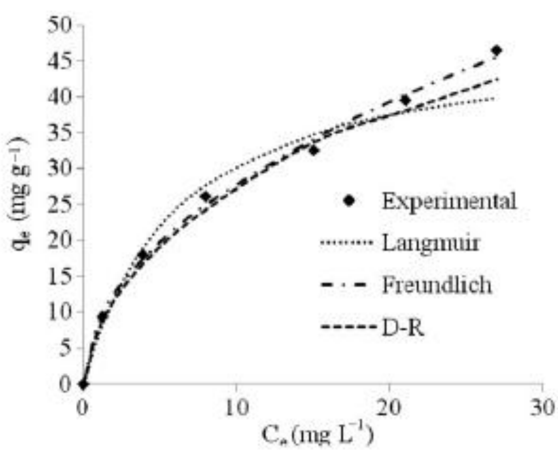

Fig.22 Langmuir and Freundlich adsorption isotherm for phenol

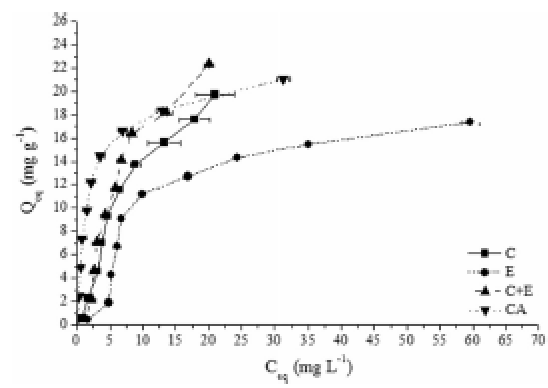

Fig.22 Langmuir isotherm for adsorption of cadmium ions

Adsorption of Cadmium metal ion using Jatropha fruits as adsorbent

Jatropha fruits were dried for fourty five days and the investigator prepared three types of adsorbent using the bark, endosperm in the seed and endosperm and seed peel together. The author dried all the above for 48 hours at 60 ^{0}C and particle size of 14 to 60 mesh size was prefered.50 mg of the biosorbent was mixed with 50 ml of potassium chloride solution at pH 2 to 9 and agitated for 24 hours at 200 rpm. The cadmium solution was prepared at different concentration and pH effects were studied. The adsorption was greater at pH 4 to 5 shown in the Fig.21.The author confirms cadmium ion removal was 86% for bark, 74% for endosperm and 82% for Endosperm and seed peel. The pseudo second order model fits with the kinetic models and R^2 value is 1.000 for bark and endosperm, 0.999 for endosperm and peel. The Langmuir model Fig.22, shows monolayer adsorption for all the three adsorbents. The constant Q=29.665mg/g for bark, Q=19.52mg/g for endosperm and Q=34.67mg/g for endosperm and peel. The Freundlich model shows R^2 = 0.991.The thermodynamic parameters for jatropha bark was ΔG=-11.962KJ/mol,ΔH=-5.87KJ/mol,ΔS= 1.158J/mol, for Endosperm ΔG= -6.28 KJ/mol, ΔH= -5.14 KJ/mol, ΔS= 5.84 J/mol, Endosperm and peel was ΔH= -12 KJ/mol, ΔS= 42.48 J/mol[41].

Conclusion

The adsorption plausibility of jatropha curcas investigated by various authors is reviewed. They have concluded that jartopha curcas is found to be an alternative source of bioremediation to sequester dyes and heavy metals from the effluent water.Remazol Brilliant blue dye showed 90% removal at pH 3 and methylene blue showed removal at increased pH 2 to 4. Acid red dye showed removal at pH 6.5 to 7.5. The heavy metal like copper was found to get adsorbed at pH 4 to 6 with 82 to 89% removal. Also phenol, cadmium ions were adsorbed using jatropha curcas as adsorbent. The adsorption isotherms Freundlich and Langmuir curves are described above.

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