Efficacy Study of Low Cost Bioadsorbents in the Removal of Target Heavy Metals

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Abstract— *The purpose of this study is to investigate the effectiveness of rice husk, saw dust and tea waste as adsorbent for the removal of cadmium, chromium and lead ions respectively. The main parameters that influenced heavy metal adsorption on bioadsorbent were adsorbent dosage, % removal and pH value. Using the initial concentrations of lead, cadmium and chromium solutions at 10 ppm, the analysis was continued using contact time 60 mins. Besides that the influences of adsorbent dosage also been studied in a range of 10mg to 30mg.After that contains of heavy metal ions were analyzed using Atomic Adsorption Spectrophotometre (AAS). The maximum % removal of cadmium is 95.7% at 20ppm of initial concentration and 20mg adsorbent dosage of rice husk at pH 6.The maximum % removal of chromium is 98.75% at 20ppm of initial concentration and 10mg adsorbent dosage of sawdust at pH 3.The maximum % removal of lead is 99.25% at 20ppm of initial concentration and 10mg adsorbent dosage of tea waste at pH 5.5 batches. The batch studies revealed that the adsorption was influenced by the initial metal concentration, the biomass dose and solution pH. Langmuir isotherm model ($R^2 \approx 1$) was used to analyze the equilibrium data.*

Keywords— Bioadsorbent , Rice husk, saw dust, tea waste , Heavy metals, Isotherms, Kinetics.

I. INTRODUCTION

The increasing concern about the contamination of water bodies by heavy metals has stimulated a large number of researches to find possible ways to remove these toxic substances from the environment. To overcome some of the limitations of physicochemical treatments, there is a need for inexpensive and efficient technology for the treatment of metal containing wastes so that metal concentration can be reduced to environmentally acceptable levels. Use of biomass for metal removal/recovery is considered to be a viable alternative to conventional methods.

Various methods such as chemical precipitation, membrane process, ion exchange, solvent extraction, electrodialysis, and reverse osmosis are adopted for removing heavy metal ions. Which are economically non viable (Demirbas, 2008) and have many disadvantages such as incomplete metal removal, high reagent and energy consumption, and generation of toxic sludge or other waste products that require disposal or treatment (Dada et al. 2013). Biosorption technique has advantages over the conventional methods, which include reusability of biomaterial, low operating cost, selectivity for specific metal, short operation time and no chemical sludge. Having functional groups including carboxyl, hydroxyl, imidazole, sulphydryl, amino, phosphate, sulfate, thioether, phenol, carbonyl and amide etc the bioadsorbents form metal complexes or chelates with the heavy metal ions. (Amin et al, 2006) In the recent years agricultural based biosorbent materials have been utilized for removal of heavy metal through biosorption technique. coconut husk and shell, sea weeds, bagasse ash, hazelnut shell, peanut hull, tree fern, black gram husk, maize leaf, maize, sun flower waste, coffee beans, Ficus religiosa leaves, wheat bran, almond shell, tea waste are used as low cost biosorption material (Qaiser, et al., 2009).with the following background the present investigation was aimed to evaluate the adsorption efficiency of selected low cost bioadsorbents tea waste, rice husk and saw dust in the removal of lead, cadmium and chromium respectively.

II. MATERIALS AND METHODS

2.1 Sampling

Adsorbents namely tea waste, rice husk and saw dust were collected from house hold chores , nearby tea stall and heavy metals water containing solution was prepared in the laboratory. Lead nitrate, Potassium dichromate and cadmium nitrate with 99.9% analytical grade was used to prepare the stock solution. Different initial concentrations of metal ions were prepared by diluting the stock solutions

2.2 Preparation of adsorbents

2.2.1 Rice Husk

Rice husk was obtained from a local mill, sieved (50–60 mesh) size, washed several times with distilled water, dried at 60°C for 2 h and preserved at room temperature. Five gram dried-husk was treated with 100 ml of 1.0 M K_2 HPO_4 for 24 h. The mixture was filtered and washed several times with distilled water to remove the excess phosphate from the treated husk. The filtrate was tested for PO^{3-} ions by the standard method. The resultant adsorbent was finally dried at 70°C for 2 h and preserved at room temperature in a sealed bottle. All the chemicals used were of analytical grade. Stock solutions (1000 mg l^{-1}) of different metal ions were prepared in distilled water using their nitrates.

2.2.2 Saw Dust

The sawdust was collected from the local saw mill and sieved through a mesh. Then, it was washed with distilled water to remove the surface adhered particles and dried at a temperature of 60-80^o C in an oven.

2.2.3 Tea Wastes

Dirt are removed from the tea wastes by washing with distilled water for much times until a colorless solution of tea waste was observed at room temperature. Decolourized and cleaned tea waste was dried to room temperature for few days and then used as adsorbents.

The initial metal concentration and the concentration of the metal remaining on the solution were determined using Atomic absorption spectrophotometer (DDC AVONTA A5182).

2.2.4 Biosorption Studies

The experiments were carried out under constant shaking of 100ml of simulated solutions in conical flasks in heavy rotatory shaking apparatus. Samples were withdrawn after a definite time interval and filtered through Whatman No. 41 filter paper and then measured in AAS.

2.3 Batch Analysis

2.3.1 Biosorption % of adsorbents for heavy metal from solution

The percentage biosorption of chromium, lead and cadmium was calculated as :

$$\textbf{Biosorption \%} = (Co - Cf) * 100/Co$$

where , Co is initial concentration of chromium, cadmium and lead in stock solution (before being mixed with the adsorbent) and Cf is the equilibrium concentration of chromium, cadmium and lead in metal solution (after being mixed with the adsorbent).

2.3.2 Adsorption isotherm of heavy metals on bioadsorbents

The adsorption study of heavy metals on bioadsorbents was carried out by batch equilibrium experiments to determine the adsorption capacity of bioadsorbents. Test were performed by agitating 10, 20, 30 mg of bioadsorbents with 10, 20, 30 ppm of heavy metal solution centrifuged at different rpm at room temperature for 60 mins. The residual metal was analyzed with an AAS.

The amount of heavy metal adsorbed Qe (mg/g) was calculated by equation:-

$$Qe = (Co - Ce)V/m$$

Where, Qe = amount of heavy metal adsorbed on adsorbent at equilibrium (mg/g) Co= initial concentration of heavy metal in solution (mg/l)

Ce= concentration of heavy metal in solution at equilibrium (mg/l)

M= mass of adsorbent used (g)

V= volume of heavy metal solution taken (ml)

III. RESULTS AND DISCUSSION

In this study, rice husk, saw dust and tea waste as the tested bioadsorbent were taken for the removal of target heavy metals like cadmium, chromium and lead respectively. Rice husk is taken for the removal and recovery of Cd as it is found to be more efficient bioadsorbent for Cd [Ajmal et. al (2001)]. Waste tea leaf is used for the removal of Pb as it may be more efficient for the target heavy metal [Shrestha et.al (2013)].Saw dust is taken for the removal of chromium as it may shows optimum adsorption efficiency [Aeisyah Abas et.al.(2013)].

The adsorption efficiency analysis of Rice husk in the removal of cadmium has been depicted in Table.1. Three different concentrations of cadmium i.e. 10, 20 and 30 ppm were choosen for biosorption at 120 rpm for 60 mins at room temperature. The maximum removal efficiency for Cd (10 ppm) is 92% at pH 6 when treated with 30 mg of rice husk, Cd (20 ppm) is 95.7 % at pH 6 when treated with 20 mg of rice husk , Cd (30 ppm) is 93.6 % at pH 6 when treated with 10 mg of rice husk.

TABLE 1
SHOWING DIFFERENT PARAMETERS ANALYSED FOR THE ADSORPTION EFFICIENCY ANALYSIS OF RICE HUSK IN THE REMOVAL OF CADMIUM.

Test no.	Initial heavy metal conc. (mg/l)	Amount of adsorbent used (mg)	Contact time (min)	Mixing speed (rpm)	pH	temp	Final heavy metal conc. (mg/l)	Biosorption %
1	10	10	60	120	6.46	37	2.39	76.1
2	10	20	60	120	6.2	37	1.49	85.1
3	10	30	60	120	6	37	0.80	92
4	20	10	60	120	6.64	37	3.91	80.45
5	20	20	60	120	6	37	0.86	95.7
6	20	30	60	120	6.76	37	1.95	90.25
7	30	10	60	120	6	37	1.90	93.6
8	30	20	60	120	6.59	37	2.83	90.5
9	30	30	60	120	6.42	37	4.25	85.83

The adsorption efficiency analysis of Saw dust in the removal of chromium has been depicted in Table 2. Three different concentration of chromium i.e. 10, 20 and 30 ppm were choosen for biosorption at 100 rpm for 60 mins at room temperature. The maximum removal efficiency for Cr (10 ppm) is 90.6% at pH 3 when treated with 30 mg of saw dust, Cr (20 ppm) is 98.75% at pH 3 when treated with 10 mg of saw dust, Cr (30 ppm) is 92.86% at pH 3 when treated with 10 mg of saw dust.

TABLE 2
SHOWING DIFFERENT PARAMETERS ANALYSED FOR THE ADSORPTION EFFICIENCY ANALYSIS OF SAW DUST IN THE REMOVAL OF CHROMIUM.

Test no.	Initia heavy metal conc. (mg/l)	Amount of adsorbent used (mg)	Contact time (min)	Mixing speed (rpm)	pH	temp	Final heavy metal conc. (mg/l)	Biosorption %
1	10	10	60	100	4.2	37	2.90	71
2	10	20	60	100	2.7	37	1.86	81.4
3	10	30	60	100	3	37	0.94	90.6
4	20	10	60	100	3	37	0.25	98.75
5	20	20	60	100	3	37	1.49	92.55
6	20	30	60	100	3.8	37	1.72	91.4
7	30	10	60	100	3	37	2.14	92.86
8	30	20	60	100	5.7	37	3.24	89.16
9	30	30	60	100	3.47	37	4.62	84.6

The adsorption efficiency analysis of tea waste in the removal of lead has been depicted in Table 3. Three different concentration of lead i.e. 10, 20 and 30 ppm were choosen for biosorption at 125 rpm for 60 mins at room temperature. The maximum removal efficiency for Pb (10 ppm) is 97.5% at pH 5.5 when treated with 10 mg of tea waste, Pb (20 ppm) is 99.25% at pH 5.5 when treated with 10 mg of tea waste, Pb (30 ppm) is 99.36% at pH 5.5 when treated with 30mg of tea waste.

TABLE 3
SHOWING DIFFERENT PARAMETERS ANALYSED FOR THE ADSORPTION EFFICIENCY ANALYSIS OF TEA WASTE IN THE REMOVAL OF LEAD.

Test no.	Initial heavy metal conc.	Amount of adsorbent used (mg)	Contact time (min)	Mixing speed (rpm)	pH	temp	Final heavy metal conc.	Biosorption %
1	10	10	60	125	5.5	37	0.25	97.5
2	10	20	60	125	4.9	37	0.39	96.1
3	10	30	60	125	5	37	0.26	97.4
4	20	10	60	125	5.5	37	0.15	99.25
5	20	20	60	125	5.3	37	0.16	99.2
6	20	30	60	125	5.4	37	0.28	98.6
7	30	10	60	125	3.5	37	7.53	74.9
8	30	20	60	125	4.5	37	3.67	87.76
9	30	30	60	125	5.5	37	0.19	99.36

3.1 Effect of Adsorbent Dosage

Figure 1 shows the relation between percentage removal of Cd and adsorbent dosage of rice husk. The percentage removal of cadmium varies at different adsorbent dosage. When 10 mg of rice husk is used for bioadsorption the maximum removal is occurs at 30 ppm concentration of cadmium i.e. 93.6%. When 20 mg of rice husk is used for bioadsorption the maximum removal is occurs at 20 ppm concentration of cadmium i.e. 95.7%. When 30 mg of rice husk is used for biosorption the maximum removal is occurs at 10 ppm concentration i.e. 92%. Optimum adsorbent dose was found to be 20mg which shows optimum removal percentage of 95.7 % at 20 ppm concentration of Cd. Results from this study describes that adsorption of Cd increases when the dose of rice husk increases and its optimum when 20 ppm concentration of Cd is treated with 20 mg of rice husk. Any further addition of the adsorbent beyond this would not cause any significant change in the adsorption due to the overlapping adsorption sites of adsorbent particles.

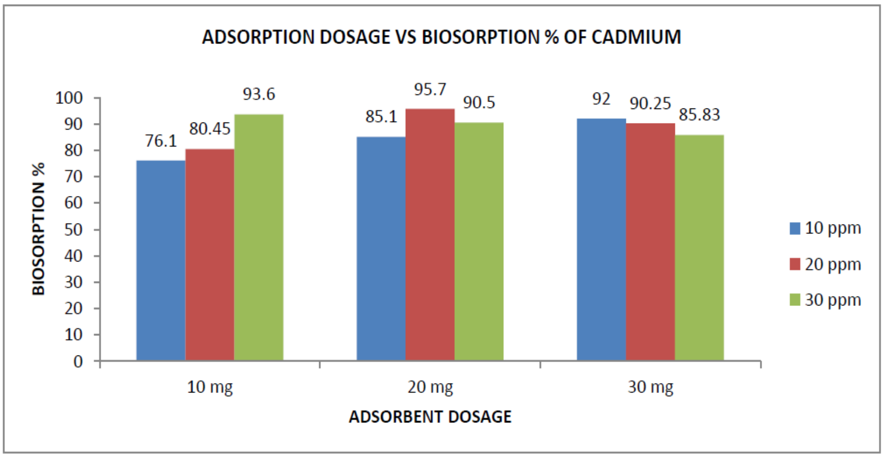

FIG.1 SHOWING THE RELATION BETWEEN PERCENTAGE REMOVAL OF CADMIUM AND ADSORBENT DOSAGE OF RICE HUSK

Figure 2 shows the relation between percentage removal of Cr and adsorbent dosage of saw dust. The percentage removal of heavy metals varies at different adsorbent dosage. . When 10 mg of saw dust is used for bioadsorption the maximum removal is occurs at 20 ppm concentration of chromium i.e. 98.75%. When 20 mg of saw dust is used for bioadsorption the maximum removal is occurs at 20 ppm concentration of chromium i.e. 92.55%. When 30 mg of saw dust is used for biosorption the maximum removal is occurs at 20ppm concentration i.e. 91.4 %. Optimum adsorbent dose was found to be 10mg which shows optimum removal percentage of 98.75 % at 20 ppm concentration of Cr. Results from this study describes that adsorption of Cr is always maximum at 20 ppm concentration in all the three adsorbent dosage of saw dust. Any further addition of the adsorbent beyond this would not cause any significant change in the adsorption due to the overlapping adsorption sites of adsorbent particles and the biopsorption percentage decreases gradually.

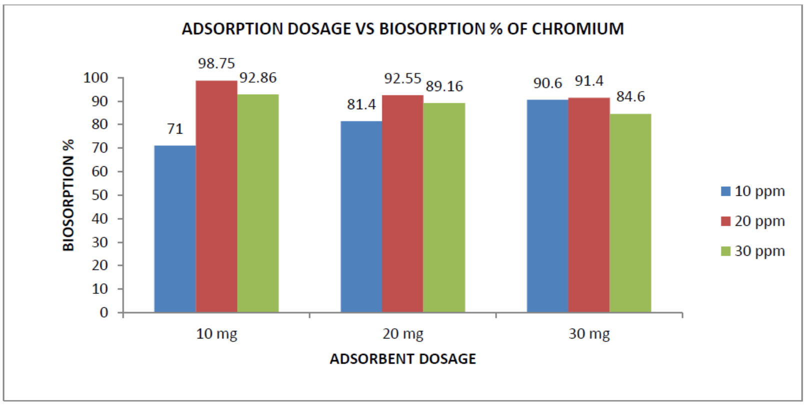

FIG.2 SHOWING THE RELATION BETWEEN PERCENTAGE REMOVAL OF CHROMIUM AND ADSORBENT DOSAGE OF SAW DUST

Figure 3 shows the relation between percentage removal of Pb and adsorbent dosage of tea waste. The percentage removal of heavy metals varies at different adsorbent dosage. When 10 mg of tea waste is used for bioadsorption the maximum removal is occurs at 20 ppm concentration of lead i.e. 99.25%. When 20 mg of tea waste is used for bioadsorption the maximum removal is occurs at 20 ppm concentration of lead i.e. 99.2%. When 30 mg of rice husk is used for biosorption the maximum removal is occurs at 30 ppm concentration i.e. 99.36%. Optimum adsorbent dose was found to be 30mg which shows optimum removal percentage of 99.36% at 30 ppm concentration of Pb.

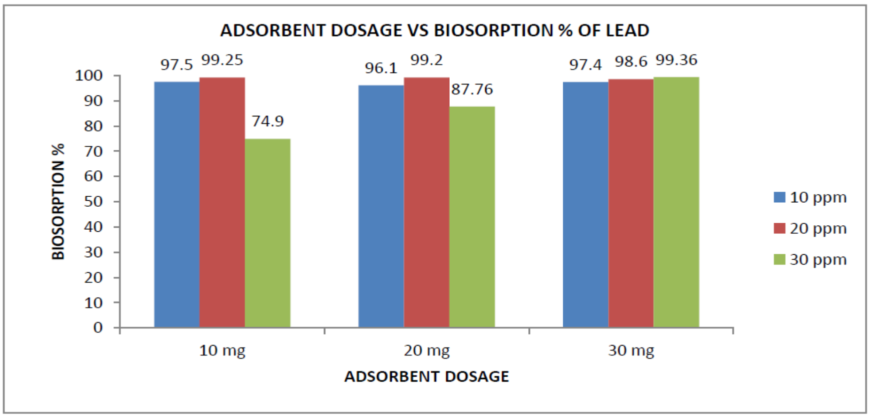

FIG.3 SHOWING THE RELATION BETWEEN PERCENTAGE REMOVAL OF LEAD AND ADSORBENT DOSAGE OF TEA WASTE

3.2 Effect of pH

The pH of the solution is an important parametre affecting adsorption of heavy metals. The effect of pH on the adsorption of Cd, Cr and Pb by rice husk, saw dust and tea waste is showed in figure 4, 5 and 6 respectively.

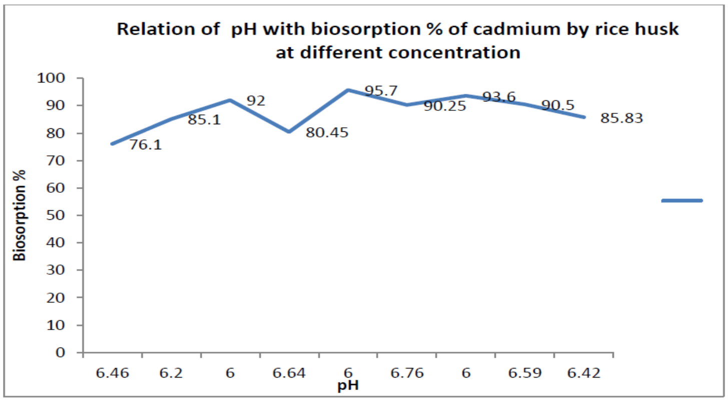

FIG.4 SHOWING THE RELATIONSHIP OF PH WITH BIOSORPTION % OF CADMIUM BY RICE HUSK AT DIFFERENT CONCENTRATION

Figure 4 shows the effect of pH on the removal of cadmium by rice husk. The maximum adsorption occurs at pH 6 for rice husk. The maximum adsorption efficiency for cadmium is 95.7%. But when the pH was increased beyond 6.0, a gradual decrease in the percentage adsorption was observed. This might be due to the net positive surface potential of the sorbent which decreased with increasing pH resulting in weakening of electrostatic force between adsorbate and adsorbent which ultimately led to the lowering of sorption capacity. The amount of adsorption increases with increasing pH upto the point 6 where the heavy metals precipitate.

Figure 5 shows the effect of pH on the removal of chromium by saw dust. The maximum adsorption occurs at pH 3 for saw dust. The maximum adsorption efficiency for chromium is 98.75%. But when the pH was increased beyond 95.73, a gradual decrease in the percentage adsorption was observed. This might be due to the net positive surface potential of the sorbent which decreased with increasing pH resulting in weakening of electrostatic force between adsorbate and adsorbent which ultimately led to the lowering of sorption capacity. The amount of adsorption increases with increasing pH upto the point 3 where the heavy metals precipitate.

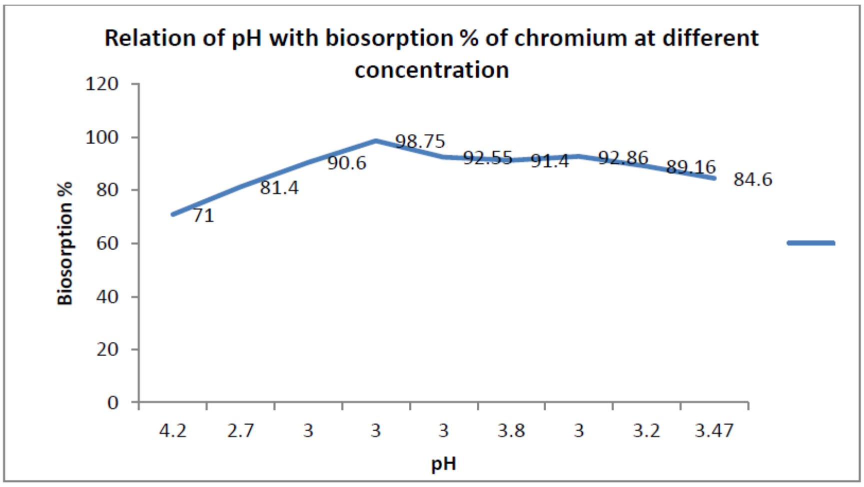

FIG.5 SHOWING THE RELATIONSHIP OF PH WITH BIOSORPTION % OF CHROMIUM BY SAW DUST AT DIFFERENT CONCENTRATION

Figure 6 shows the effect of pH on the removal of lead by tea waste. The maximum adsorption occurs at pH 5.5 for tea waste. The maximum adsorption efficiency for lead is 99.25%. But when the pH was increased beyond 5.5, a gradual decrease in the percentage adsorption was observed. This might be due to the net positive surface potential of the sorbent which decreased with increasing pH resulting in weakening of electrostatic force between adsorbate and adsorbent which ultimately led to the lowering of sorption capacity. The amount of adsorption increases with increasing pH upto the point 5.5 where the heavy metals precipitate.

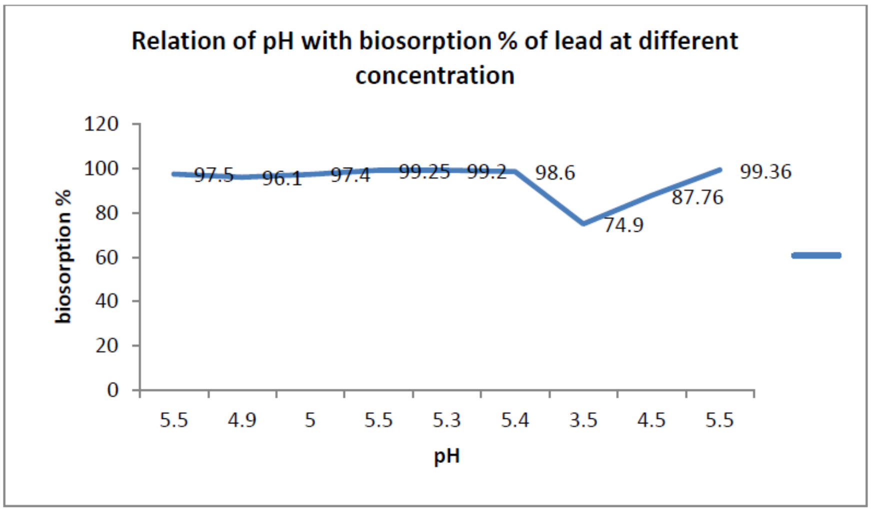

FIG.6 SHOWING THE RELATIONSHIP OF PH WITH BIOSORPTION % OF LEAD BY TEA WASTE AT DIFFERENT CONCENTRATION

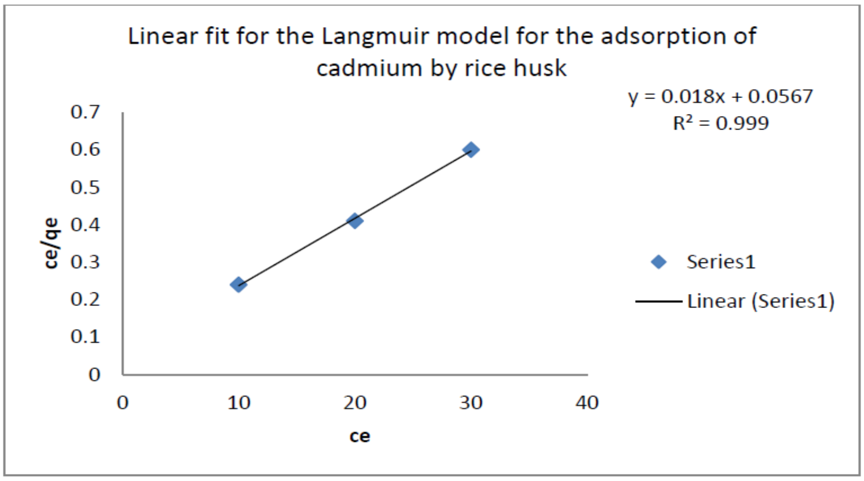

FIG.7. SHOWING LANGMUIR MODEL FOR CADMIUM REMOVAL BY RICE HUSK

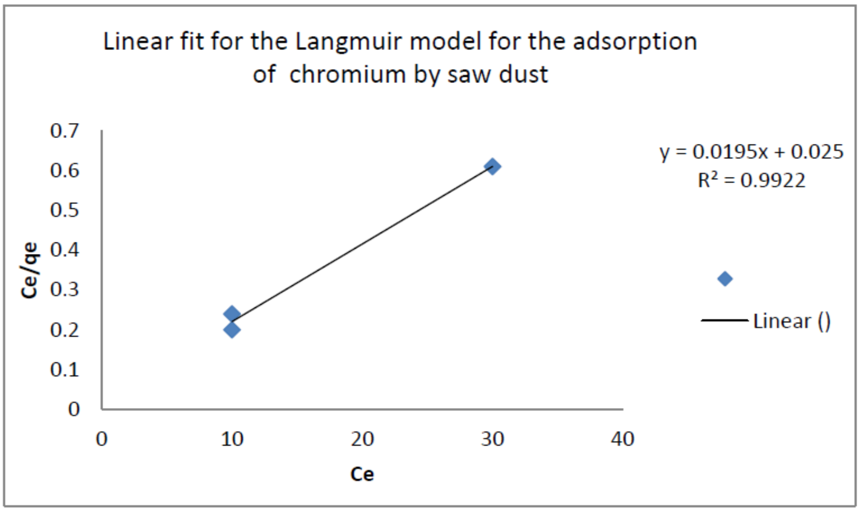

FIG.8. SHOWING LANGMUIR MODEL FOR CHROMIUM REMOVAL BY SAW DUST

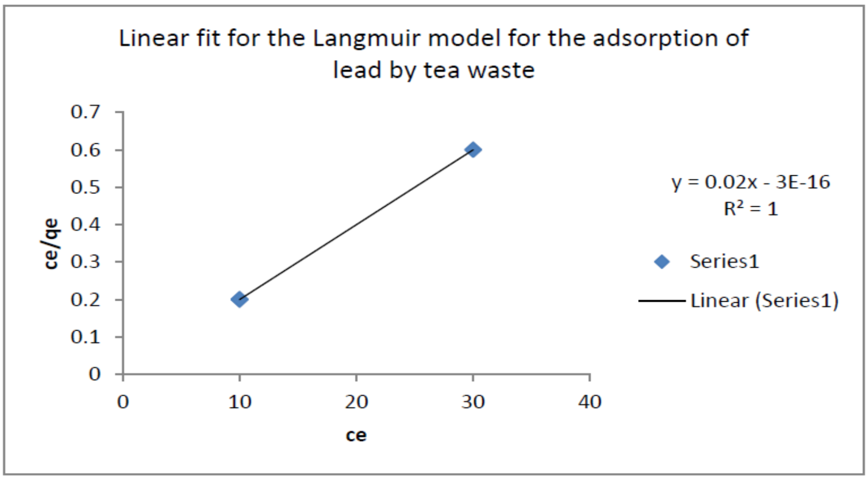

FIG.9. SHOWING LANGMUIR MODEL FOR LEAD REMOVAL BY TEA WASTE

3.3 Langmuir Adsorption Isotherm Model

The adsorption isotherms were evaluated using the linearized Langmuir model by :-

$$Ce / qe = 1/ qm\,b + Ce / qm$$

where Ce (mg/L) is equilibrium concentration of the adsorbate, qe (mg/L) adsorption capacity adsorbed at equilibrium , qm (mg/g) is the maximum adsorption capacity and b (L/mg) is the binding constant. Langmuir parameters qm and b were calculated from the plot of Ce/qe versus Ce. Langmuir parameters and correlation coefficients are given in Table 4. The high value of Langmuir correlation coefficient confirmed that the Langmuir isotherm model is best fitted.

TABLE 4
SHOWING LANGMUIR PARAMETERS AND CORRELATION COEFFICIENTS

Metal ions	qm (mg/g)	Temp °C	b (L/mg)	R^2
Cadmium	95.7	37	0.056	0.999
Chromium	98.75	37	0.025	0.992
Lead	99.25	37	0	1

IV. CONCLUSION

In present work attempt have been made for studying the removal of heavy metals like cadmium, chromium and lead by low cost adsorbent like rice husk, saw dust and tea waste respectively. The major findings of the study are discussed in this section.

Batch studies on cadmium, chromium and lead removal showed significant effects of the variables adsorbent dose, initial metal concentration, pH. The results provide a good indication of the different operating conditions that would be required for efficient removal of each heavy metal from aqueous solution. Adsorbent dose is a significant factor in adsorbtion process since the percentage removal of heavy metals varies at different adsorbent dosage. When 10 ppm of initial heavy metal concentration is taken into consideration the optimum adsorbent dose was found to be 30mg in both the cases which shows optimum removal percentage of 92 % and 90.6 % in case of Cd and Cr respectively. While in case of lead initial adsorbent dose of 10 mg of tea waste shows optimum adsorption of 97.5 %. When 20 ppm of initial heavy metal concentration is taken into consideration the optimum adsorbent dose was found to be 10mg in both the cases which shows optimum removal percentage of 98.25 % and 99.25 % in case of Cr and Pb respectively. While in case of Cd adsorbent dose of 20 mg of rice husk shows optimum adsorption of 95.7 %. When 30 ppm of initial heavy metal concentration is taken into consideration the optimum adsorbent dose was found to be 10mg in both the cases which shows optimum removal percentage of 93.6 % and 92.86 % in case of Cd and Cr respectively. While in case of Pb adsorbent dose of 30 mg of tea waste shows optimum adsorption of 99.36%. pH is also a significant factor in adsorbtion process since it causes electrostatic changes in the solution. At pH 6 of rice husk shows maximum adsorption efficiency for cadmium is 95.7%, for chromium at pH 3 of saw dust shows maximum adsorption efficiency 98.75% and for lead at pH 5.5 of tea waste shows maximum adsorption efficiency 99.25. Langmuir isotherm were observed to fit the equilibrium data and the model parameters were calculated using linearized equations. Langmuir isotherm model $R^2 \sim 1$ is in good agreement with the experimental data. These experimental results revealed that Rice husk can be used as an efficient bioadsorbent for the removal of Cd, Saw dust can be used as an efficient bioadsorbent for the removal of Cr and Tea leaves can be used as an efficient bioadsorbent for the removal of Pb

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