Asian Journal of Chemistry; Vol. 24, No. 6 (2012), 2425-2432

ASIAN JOURNAL OF CHEMISTRY

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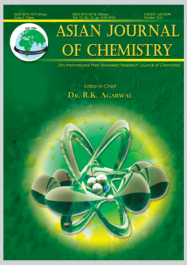

Studies of Biosorption of Heavy Metals in Soil by Using Rice Straw

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(*Received*: 4 April 2011; *Accepted*: 6 January 2012) AJC-10918

Adsorption experiments were carried out using waste rice straw as a biosorbent to adsorb Cd, Pb, Cr, Co, Ni and Cu at room temperature from agricultural soil irrigated with industrial waste water. Estimation of metals was done by atomic absorption spectroscopy. The main objective was to determine (I) appropriate adsorption isotherm of heavy metals and (II) adsorption efficiency of heavy metals on rice straw. Metal removal efficiency of rice straw was observed after 8 and 30 days by varying the amount of biosorbent. Eight days equilibrium studies showed that Langmuir isotherm provided the best correlation for Ni, Cu and Co while after 30 days the studies gave the Langmuir isotherm correlation with Cd, Pb. Ni and Cr. Similarly Pb, Cd, Cu, Co and Cr followed Freundlich isotherm. Nickel had highest adsorption capacity on to rice straw. Estimation of nitrates, sulphates and phosphates were done by using UV-Visible spectrophotometer. X-ray diffraction studies were also done, which indicates the presence of SiO_2 and Muscoit mineral.

Key Words: Biosorption, Equilibrium studies, Rice straw.

INTRODUCTION

Soil science is the study of soil as natural resource on the surface of the earth including soil formation, classification and mapping; physical, chemical, biological and fertility properties of soils and these properties in relation to the use and management of soils[1]. Soil is a natural body consisting of layers (soil horizons) of mineral constituents of variable thickness, which differ from the parent materials in their morphological, physical, chemical and mineralogical characteristics[2]. Mining, manufacturing and the use of synthetic products can result in heavy metal contamination of urban and agricultural soils. Potentially contaminated soils may occur at old landfill sites (particularly those that accepted industrial wastes), old orchards that used insecticides containing arsenic as an active ingredient, fields that had past applications of waste water or municipal sludge, areas in or around mining waste piles and tailings, industrial areas where chemicals may have been dumped on the ground, or in areas downwind from industrial sites. Excess heavy metal accumulation in soils is toxic to humans and other animals. Acute (immediate) poisoning from heavy metals is rare through ingestion or dermal contact, but is possible. Chronic problems associated with long-term heavy metal exposures are lead which causes mental lapse and cadmium that affects kidney, liver and GI tract. The most common problem causing cationic metals (metallic elements whose forms in soil are positively charged cations *e.g.*, Pb^{2+}) are mercury, cadmium, lead, nickel, copper, zinc, chromium and manganese[3]. The most common anionic groups (elements having negative charge *e.g.*, MoO_4) are arsenic, selenium and boron[4].

Research has demonstrated that plants are effective in cleaning up contaminated soil[5]. The assessment of meal-binding capacity of some biomass has gained momentum since 1985. Indeed some biomass types are very effective in accumulating heavy metals. Availability is the major factor to be taken in to account to select biomass for the cleanup purpose. The economy of environmental remediation dictates that biomass must come from the nature or even has to be the waste material. Cost effectiveness is the main attraction for the metal biosorption and it should be kept that way[6].

Siegel e*t al.*[7] used filamentous fungi as heavy metal pollutant[7]. Similarly Liu *et al.*[8] used thiobacillus thiooxidans for biosorption of Zn(II), Cu(II) and of the binary mixture of these two metal ions. Removal of cadmium, lead and nickel from industrial waste water has been investigated by using tea waste as a natural adsorbent. Results indicate that removal efficiency is highest for lead and lowest for cadmium[9]. Pehlivan *et al.*[10] investigated the potential to remove Cu^{2+} and Pb^{2+} ion from aqueous solutions through biosorption using barley straw in batch experiments. Equilibrium isotherms have been measured and modelled. The adsorption data fit well with the Langmuir isotherm model[10]. Ability of bael tree leaf powder to adsorb nickel from aqueous solution has been reported by Kumar and Kirthika[11]. The experimental isotherm data were analyzed using the Langmuir, Freundlich and Temkin equations. Adsorption of chromium on wheat bran using adorption techniques has also been reported[12]. Tan *et al.*[13] succeeded in removing signi-ficant amount of Cr(III) using husk fibre and rice straw from aqueous solution. The adsorption capacity for lead, copper and cadmium on biomass increased with increasing temperature[14].

In this study, rice straw is used as a biosorbent to adsorb heavy metals from the soil irrigated with industrial wastewater because of its low cost and friendly environment. Rice straw is a lignocellulosic agricultural byproduct containing cellulose (37.4 %), hemi-cellulose (44.9 %), lignin (4.9 %) and silicon ash (13.1 %)[15]. Metal ions are bounded to lignocellulosic biosorbents through chemical functional groups[16]. Phosphoric acid modified rice straw showed high ability for dyes removal from aqueous solution[17].

EXPERIMENTAL

All reagents used were of analytical grade.

Sampling procedure: Soil samples were collected directly from the industrial area. About 1 kg of soil was taken from a depth of 0-10 cm and kept in separate containers, which were air tight to prevent contamination from environment. Soil samples were taken in stainless steel beakers and heated in an electric oven at 110 ºC for 3-4 h. After drying the samples were crushed or grinded in a sand stone disc grinder with 180 mm mesh size to bring the samples in powdered form.

Preparation of biosorbent: The rice straw was collected. It was cut to small pieces and dried in an oven. The dried rice straw was then crushed in a crusher to small pieces and sieved.[12]

Preparation of samples: Samples were prepared by taking different amounts of rice straw. The samples were then kept for 8 and 30 days. The effect of biosorbent dosage and time on biosorption process was studied[12].

Three samples were prepared by taking 10 g of soil. 0.5, 1.0 and 2.0 g biosorbent (rice straw) was added in each of these samples and then stirred for 1 h. Similarly 3 more samples were prepared in the similar way mentioned above and kept for 30 days. The soil samples were digested by the nitric acid extraction method[18]. In nitric acid digestion method 2.5 g of soil sample was put in to an Erlenmeyer flask and added 2.5 mL of conc. HNO_3 and 5 mL of distilled water was added in it. The mixture in the flask was kept for 24 h. After 24 h, distilled water was added to the mixture to reach 25 mL. The extract was filtered through Whatman No.42 paper. The reference material was extracted with the same exactant volume in four replicates[19]. The absorbance of the sample was recorded and the amount of metal in the soil sample solution was estimated by atomic absorption spectrophotometer (Hitachi Zeeman-8000).

Estimation of nitrates in soil by spectroscopic method: 10 g of soil sample (dried) was mixed with 100 mL distilled water and stirred for 10 min. 1 g calcium carbonate was added to avoid loss of nitrates. Then the sample was again stirred for 20 min and filtered by whatman filter paper no. 42 in 100 mL flask.

Removal of chloride ion from soil extract: 50 mL of the soil extract was transferred to a 50 mL beaker. Acetic acid was added to this soil extract to maintain pH at 4-5. Then silver nitrate solution was added for complete precipitation. Precipitates were filtered, washed and made the volume upto the mark with dilute acetic acid solution.

Procedure for standard curve: 50 mL sodium nitrate (0.4 mg of NO_3^- per mL) stock solution was evaporated to dryness. When cold, 2 mL of phenolphthalein sulphonic acid was added and transferred it to a 500 mL volumetric flask and made the volume up to the mark with distilled water. From this stock solution 10 standards were prepared in 25 mL volumetric flask with a difference of 0.5 mL. Ammonia solution was added to make these solutions alkaline and then absorbance was recorded at 420 nm.

Analysis of soil extract: 10 mL chloride ion free soil extract was evaporated to dryness in a china dish on water bath. When cold, 2 mL of phenolphthalein sulphonic acid was added to form complex with nitrate. It was diluted with distilled water previously cooled in ice bath. Yellow colouration was obtained when made alkaline with NH_3 solution. Then it was transferred to 25 mL measuring flask and volume was made up to the mark with dilute ammonia. Absorbance was noted at 420 nm on spectrophotometer (U-2800 Hitachi, Japan)[18].

Estimation of phosphates in soil by spectroscopic methods:

Sample preparation: Soil sample was heated overnight at 50 ºC. 50 mL of water was taken in 250 mL measuring flask, 0.75 g of ammonium sulphate was dissolved in it. To this 5 mL of concentrated sulphuric acid was added slowly. The solution gets hot. Allowed it to cool and then diluted up to the mark with distilled water. 10 g of soil and 200 mL of sulphuric acid/ammonium mixture were taken in a flask, shaked for 30 min and the solution was then filtered. The solution was clear, slightly brown in colour .

Preparation of standards: 300 ppm standard solution of phosphate was prepared by taking 0.220 g of solid KH_2PO_4 in to 500 mL measuring flask and diluted it to the mark. From this 300 ppm solution, phosphate solutions having concentrations 3,6,12 and 15 ppm were prepared.

Preparation of complex: For this purpose, in 500 mL volumetric flask 5 g of ammonium molybdate was dissolved in 100 mL of water. Then 160 mL of conc. H_2SO_4 was added slowly, flask becomes hot, it was cooled for 15 min and made the volume up to the mark with distilled water. 10 mL sample was taken in a 150 mL conical flask. Then 20 mL of water, 2 mL of molybdate solution and a spatula of ascorbic acid crystals was added in it. Heated the mixture slowly to boiling (a deep blue/green colour developed) and then allowed it to cool. This was repeated for all the standards. The samples were then placed in silica cells and absorbance was noted[20] at 650 nm on a spectrophotometer (U-2800 Hitachi, Japan).

Estimation of sulphates in soil by spectrophotometric method: In 50 mL Erlenmeryre flask.10 g of air dried, sieved soil was taken. Then 25 mL of acidified ammonium acetate was added and shacked for 30 min at 200 oscillations per minute. 0.25 g of activated charcoal was then added, shacked again for 3 min and filtered.

Preparation of standards: By taking different proportions of the appropriate extracting solution (20, 40, 60, 80, 100 mg/L) and 100 mg/L standard solution (0.543 g of K_2SO_4 was dissolved in the extracting solution (acidified with ammonium acetate) in one liter volumetric flask and made the volume up to the mark with more extracting solution) different standards were prepared. Then 0.25 g of activated carbon was added to these standard solutions, shaked for 3 minutes and then filtered.

10 mL of the filtrate from extracting process and 1 mL of acid seed solution (20 ppm S in 5.8 M HCl) was taken in 50 mL Erlenmeyer flask. The solution was swirled and then 0.5 g of $BaCl_2.2H_2O$ was added in it. Mixture was then allowed to stand for one minute. Absorbance of the sample solution and standards was observed at a wavelength of 420 nm by using spectrophotometer (U- 2800 Hitachi, Japan)[21].

Equilibrium studies were also by using most widely used langmiur and Freundlich isotherm models. X-ray diffraction studies were also done (D_8 Discover Bruker, Germany).

RESULTS AND DISCUSSION

Soil samples were digested by nitric acid extraction method and the concentration of metal ion in soils sample was determined by atomic absorption spectrophotometer.

Metal removal at any instant of time was also determined. Result of % age removal of metals after 8 and 30 days by 0.5, 1 and 2 g rice straw is shown in Table-1. Data shows that rice straw has highest adsorption efficiency for nickel. The adsorption efficiency of rice straw is as follows:

Ni > Co > Pb > Cu > Cr > Cd

TABLE-1
PERCENTAGE REMOVAL OF HEAVY METALS WITH RICE STRAW AFTER 8 AND 30 DAYS

Metals	% Removal after 8 days			% Removal after 30 days		
	0.5 g rice straw	1 g rice straw	2 g rice straw	0.5 g rice straw	1 g rice straw	2 g rice straw
Cd	2.37	6.72	7.51	9.09	16.02	21.00
Pb	3.92	8.93	19.45	53.17	61.38	67.00
Cu	3.80	2.86	5.71	20.95	26.6	42.85
Ni	10.23	11.36	20.45	97.3	98.86	99.62
Co	5.56	7.94	17.06	78.17	80.55	86.11
Cd	3.77	5.66	6.92	10.69	13.2	18.2

Equilibrium study: Modeling of equilibrium data was done using most widely used Langmuir and Freundlich isotherm models. The Langmuir isotherm is given by:

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

where, q_m and K_L are Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively.

The constants in the Langmuir isotherm were determined by plotting ($1/q_e$) *versus* ($1/C_e$) and making use of above equation rewritten as:

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

The plot of $1/q_e$ *versus* $1/C_e$ is linear.

The Freundlich isotherm is represented by:

$$q_e = K_f C_e^{1/n}$$

The logarithmic form of the equation becomes

$$\log q_e = \log K_f + 1/n \log C_e$$

where K_f and n are the Freundlich constants, the characteristics of the system. K_f and n are the indicators of the adsorption capacity and adsorption intensity, respectively. The plot of log Ce *vs* log q_e was employed to generate the intercept value of K_f and slope of n. The magnitude of K_f and n show easy separation of metal ions and indicate favourable adsorption. The intercept K_f value is an indication of adsorption capacity of the adsorbent. The slope 1/n indicates the effect of concentration on the adsorption capacity and represents adsorption intensity[22]. The Langmiur and Freundlich adsorption isotherm data were given in Tables 2 and 3.

TABLE-2
ISOTHERMS MODEL CONSTANTS AND CORRELATION COEFFICIENT FOR ADSORPTION OF HEAVY METALS AFTER 8 DAYS

Metals	Langmiur constants			Fruendlich constants		
	q_m (mg/g)	K_L (L/mg)	R^2	n	K_f	R^2
Cd	7.555×10^{-3}	0.040	0.980	1.273	15.847	0.005
Pb	0.923	0.102	0.998	0.664	154.470	0.975
Ni	0.102	0.337	0.617	0.264	62.490	0.462
Cu	12.576	7.88×10^{-3}	0.480	0.886	10.859	0.775
Co	1.325	0.092	0.128	0.886	10.859	0.193
Cr	2.831×10^{-3}	0.065	0.999	0.058	13615.99	0.991

TABLE-3
ISOTHERM MODELS CONSTANTS AND CORRELATION COEFFICIENTS FOR ADSORPTION OF HEAVY METALS AFTER 30 DAYS

Metals	Langmuirs constants			Freundlich constants		
	q_m (mg/g)	K_L (L/mg)	R^2	n	K_f	R^2
Cadmium	0.14	0.33	0.8136	0.28	37.04	0.866
Lead	4.61	0.086	0.9494	0.30	81.67	0.9937
Nickel	1.23	1.33	0.9801	0.37	17.38	0.9549
Copper	0.467	0.53	0.8093	0.549	1.865	0.8005
Cobalt	0.022	0.66	0.9872	0.106	85.62	0.9395
Chromium	7.76	20.13	0.9857	1.43	31.54	0.9952

Fig. 1(a) and 1(b) shows Langmuir adsorption isotherm for Cd(II) on rice straw after 8 and 30 days respectively. It seems that adsorption follows Langmuir isotherm well. The correlation coefficients were 0.980 and 0.8136. q_m and K_L were found to be $7.559 \times 10^{-}3$ mg/g and 0.040 L/mg after 8 days whereas after 30 days the values were 0.14 mg/g and 0.33 L/mg respectively.

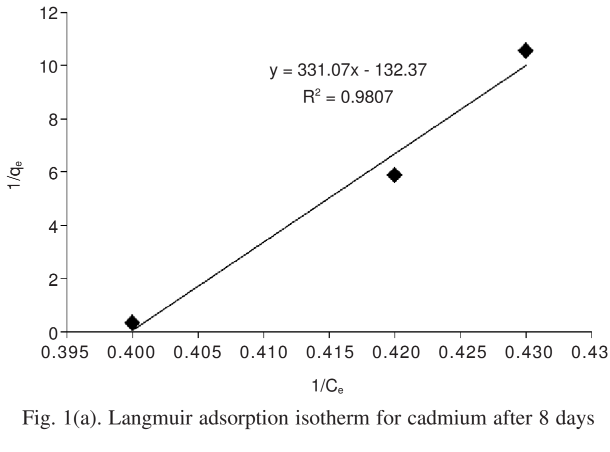

Fig. 1(a). Langmuir adsorption isotherm for cadmium after 8 days

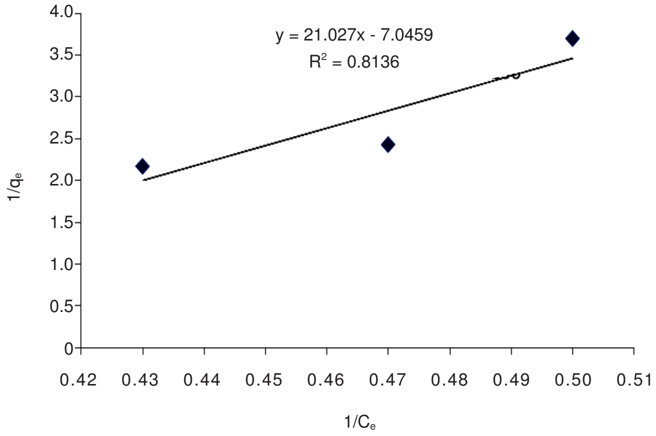

Fig. 1(b). Langmuir adsorption isotherm for cadmium after 30 days

Fig. 2(a) and 2(b) shows the Freundlich linear plot for Cd(II) after 8 and 30 days respectively. The correlation coefficient for 8 and 30 days were 0.005 and 0.866. The correlation coefficient values indicate that equilibrium adsorption data fit well to Freundlich isotherm only for 30 days. K_f and n were calculated and found to be K_f = 15,847, 37.04 and n = 1.273 and 0.28, respectively.

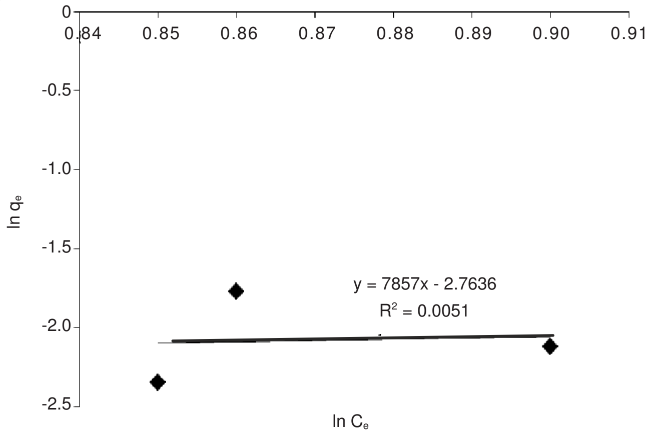

Fig. 2(a). Freundlich adsorption isotherm for cadmium after 8 days

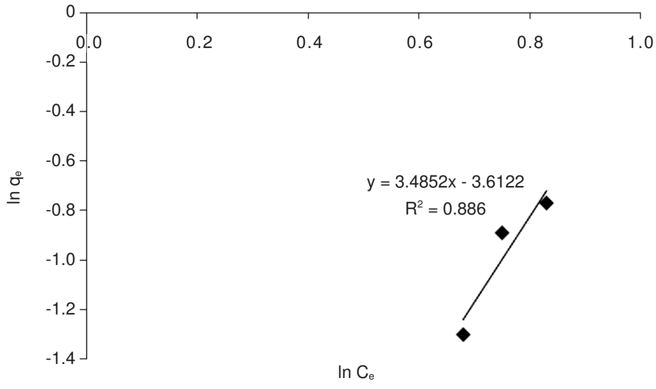

Fig. 2(b). Freundlich adsorption isotherm for cadmium after 30 days

The Langmuir plot for Pb(II) after 8 and 30 days is graphically presented in Fig. 1(c) and 1(d) respectively. The correlation coefficients were found to be 0.998 and 0.9494 for both 8 and 30 days. q_m were found to be 0.923 mg/g and 4.61 mg/g and K_L were 0.102 L/mg and 0.086 L/mg respectively.

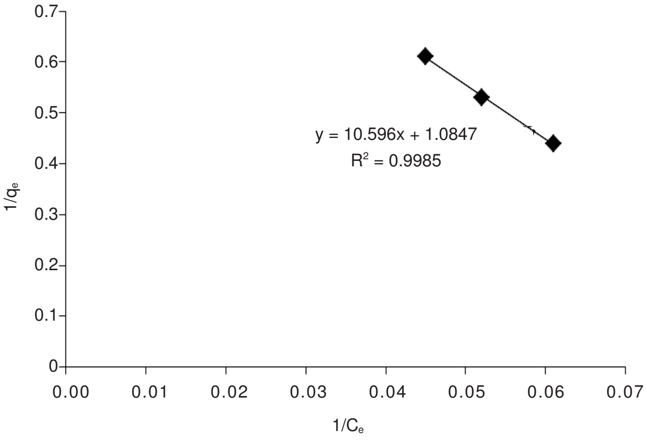

Fig. 1(c). Langmuir adsorption isotherm for lead after 8 days

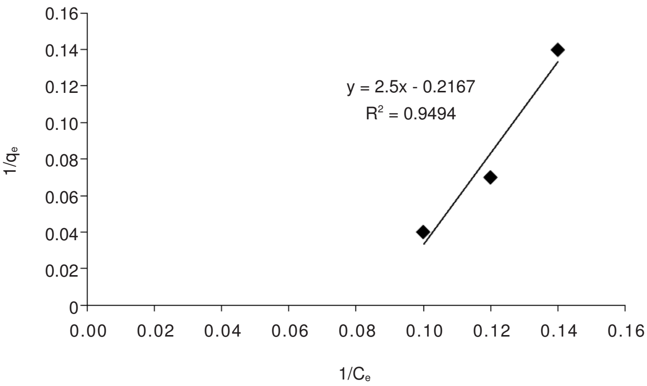

Fig. 1(d). Langmuir adsorption isotherm for lead after 30 days

Fig. 2(c) and 2(d) shows the Freundlich linear plot for Pb(II) after 8 and 30 days. The correlation coefficients were 0.975 and 0.9937. The correlation coefficient values indicate that adsorption data fit well with Freundlich isotherm. K_f and n were calculated and found to be K_f = 15.847, 81.67 and n = 0.664 and 0.30, respectively.

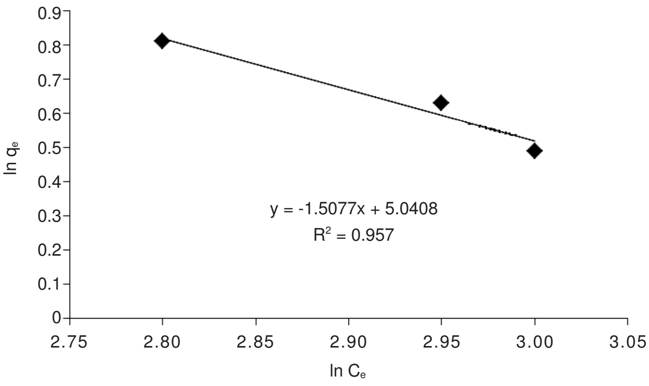

Fig. 2(c). Freundlich adsorption isotherm for lead after 8 days

Fig. 1(e) and 1(f) shows Langmuir adsorption isotherm for Cu(II) after 8 and 30 days. The correlation coefficients were 0.480 and 0.8093 respectively. q_m and K_L was found to be 12.576 mg/g and 7.88×10^{-3} for 8 days and were 0.467 mg/g and 0.53 L/mg respectively for 30 days. 8 Days data is not fitted well with langmiur isotherm.

The Freundlich plot for Cu(II) after 8 and 30 days is graphically presented in Fig. 2(e) and 2(f). The correlation

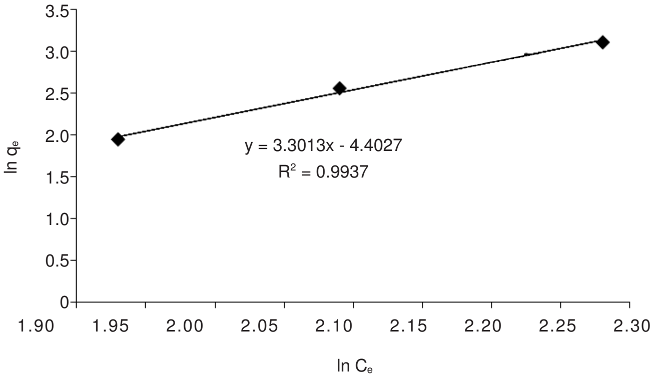

Fig. 2(d). Freundlich adsorption isotherm for lead after 30 days

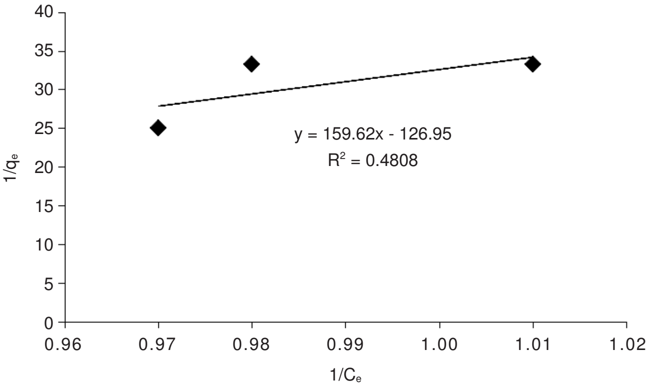

Fig. 1(e). Langmuir adsorption isotherm for copper after 8 days

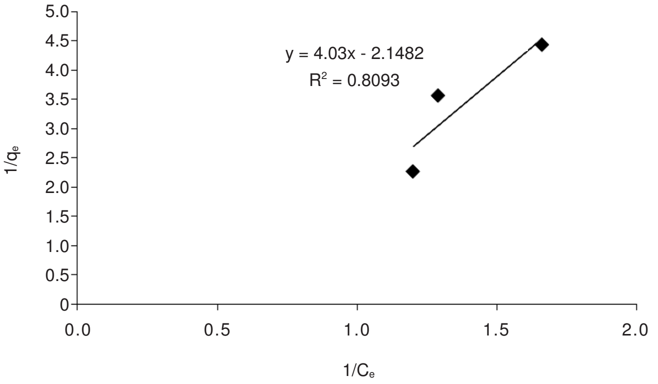

Fig. 1(f). Langmuir adsorption isotherm for copper after 30 days

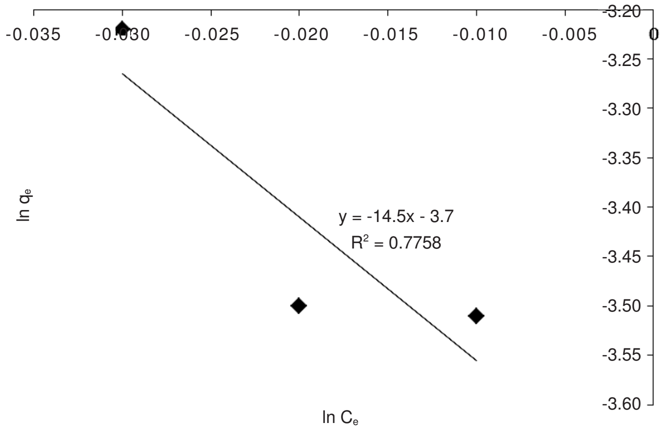

Fig. 2(e). Freundlich adsorption isotherm for copper after 8 days

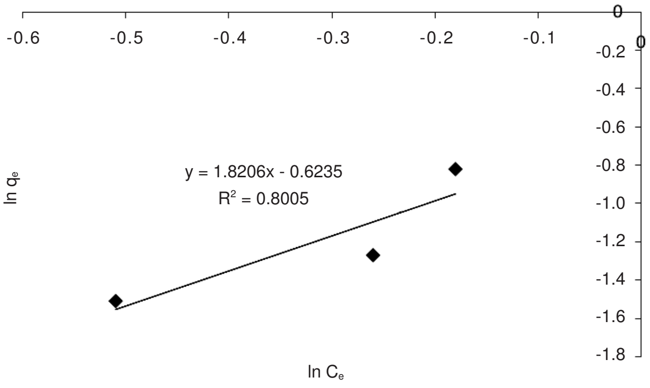

Fig. 2(f). Freundlich adsorption isotherm for copper after 30 days

coefficients were 0.775 and 0.8005. The correlation coefficient and constant values indicate that Langmuir and Freundlich isotherm fitted well with both 8 and 30 days adsorption data. K_f and n were calculated and found to be K_f = 10.859, 1.865 and n = 0.886 and 0.549, respectively.

Fig. 1(g) and 1(h) shows Langmuir adsorption isotherm for Ni(II) after 8 and 30 days. The correlation coefficients were 0.617 and 0.9801. q_m and K_L were found to be for 8 days were 0.102 mg/g, 1.33 L/mg and for 30 days were 0.337 mg/g and 1.23 mg/g respectively.

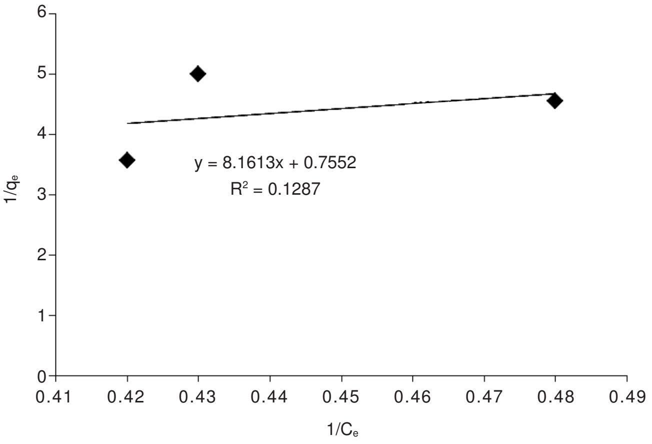

Fig. 1(g). Langmuir adsorption isotherm for nickle after 8 days

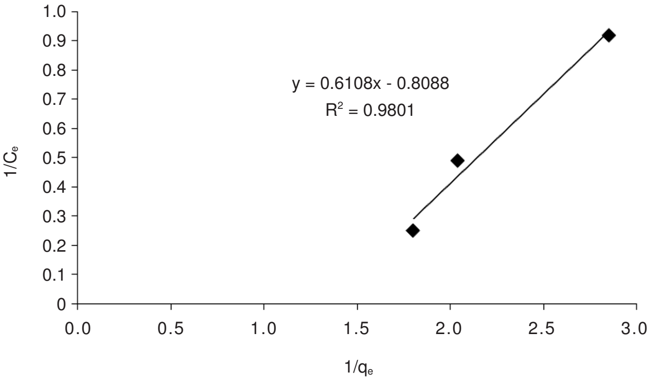

Fig. 1(h). Langmuir adsorption isotherm for nickel after 30 days

The Freundlich plot for Ni(II) is graphically presented in Fig. 2(g) and 2(h) for 8 and 30 days. The correlation coefficients were 0.462 and 0.9549. These values indicate that adsorption data fit Langmuir isotherm well. K_f and n were calculated and found to be K_f = 62.490, 17.38 and n = 0.264 and 0.37, respectively.

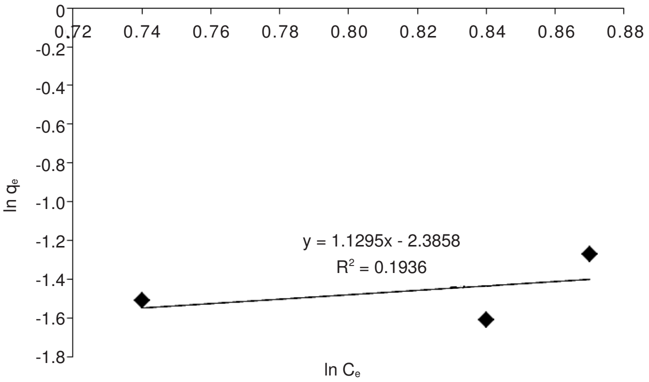

Fig. 2(g) Freundlich adsorption isotherm for nickel after 8 days

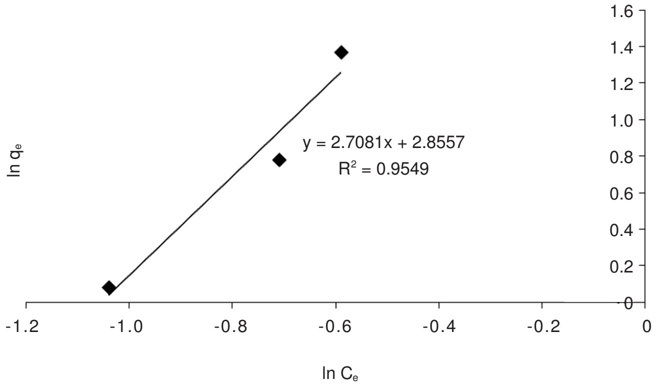

Fig. 2(h). Freundlich adsorption isotherm for nickel after 30 days

The Langmuir plot for Co(II) after 8 and 30 days is graphically presented in Fig. 1(i) and 1(j). The values of correlation coeffiecent were 0.193 and 0.9872. q_m and K_L were found to be 0.022 mg/g, 1.325 mg/g and 0.092 L/mg and 0.66 L/mg for 8 and 30 days respectively. Cobalt has the lowest adsorption capacity (q_m) for all the six metal ions.

Fig. 2(i) and 2(j) shows the Freundlich linear plot for Co(II) after 8 and 30 days. The correlation coefficients were 0.193 and 0.9395. The correlation coefficient values indicate that both adsorption data fit Langmuir isotherm well. K_f and n were calculated and found to be K_f = 10.859, 85.62 and n = 0.866, 0.106, respectively.

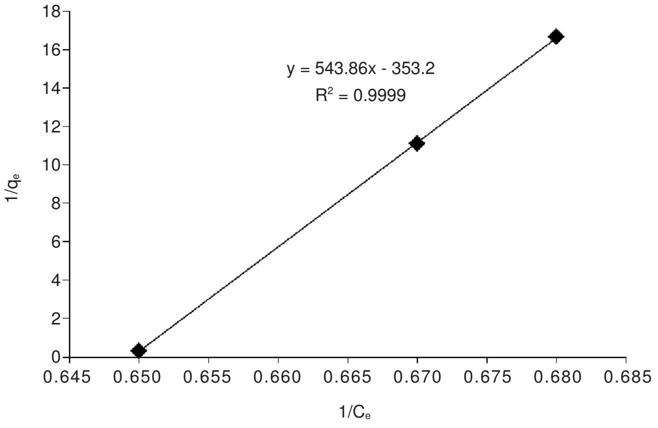

Fig. 1(i). Langmuir adsorption isother for cobalt after 8 days

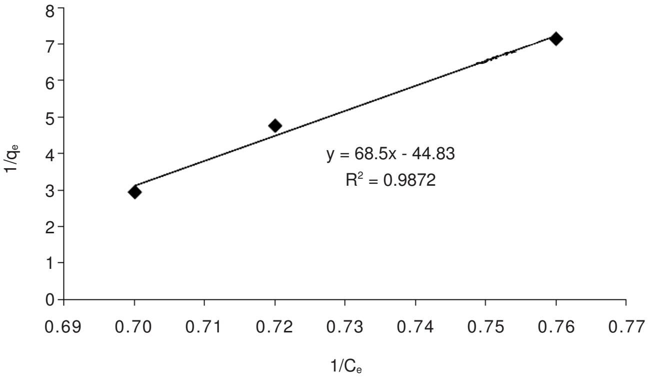

Fig. 1(j). Langmuir adsorption isotherm for cobalt after 30 days

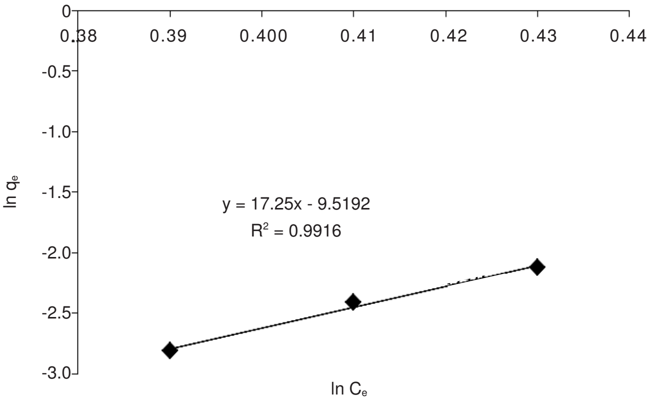

Fig. 2(i). Freundlich adsorption isotherm for cobalt after 8 days

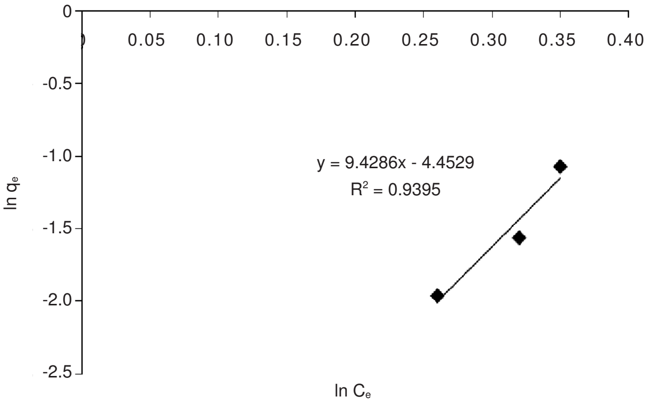

Fig. 2(j). Freundlich adsorption isotherm for cobalt after 30 days

The Langmuir adsorption isotherm Fig. 1(k) and 1(l), data of 8 and 30 days shows that for Cr(II) correlation coefficients values were 0.999 and 0.9857. q_m and K_L were found to be 7.76 mg/g, 2.831×10^{-3} mg/g and 0.0675 L/mg, 20.13 L/mg respectively. Cr(II) has highest adsorption capacity (q_m) than Cd(II), Pb(II), Ni(II),Cu(II), Co(II).

Fig. 2(k) and 2(l) shows the Freundlich linear plot for Cr(II) for 8 and 30 days. The correlation coefficients were 0.991and 0.9952.The correlation coefficient values of both indicate that adsorption data fit Freundlich isotherm well. K_f and n were calculated and found to be K_f = 13615.99, 31.54 and n = 0.058, 1.43, respectively. According to Kadirvelu and Namasivan[23], n values between 1 and 10 represent beneficial adsorption. For chromium the Freundlich isotherm fitted well with correlation coefficient of 0.9952.

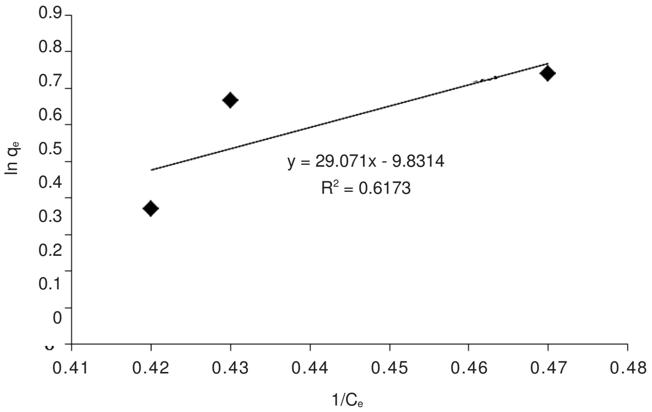

Fig. 1(k). Langmuir adsorption isotherm for chromium after 8 days

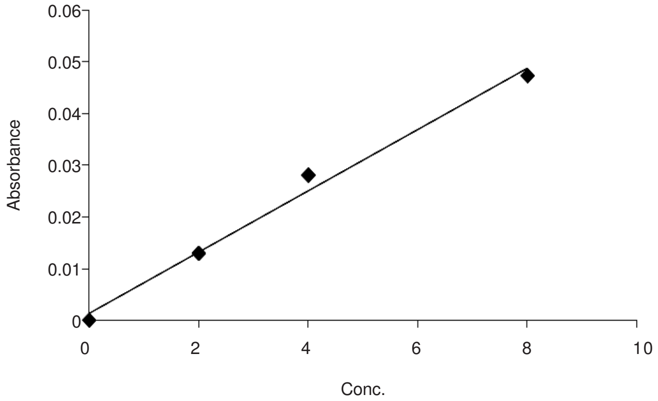

Fig. 1(l). Langmiur adsorption isotherm for chromium after 30 days

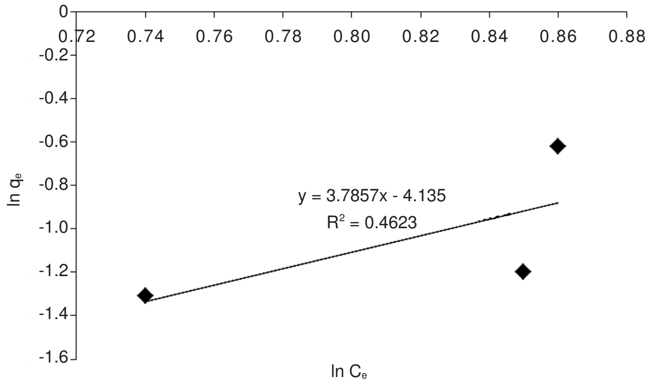

Fig. 2(k). Freundlich adsorption isotherm for chromium after 8 days

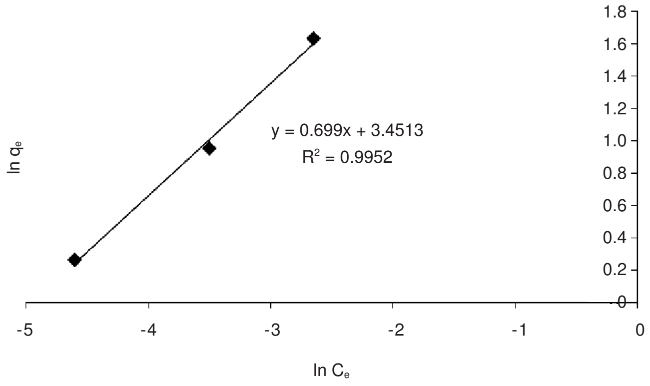

Fig. 2(l) Freundlich adsorption isotherm for chromium after 30 days

Nitrates, phosphates and sulphates in soil were determined by UV-Visible spectrophotometer. The amount of nitrates in soil was 0.146 mg, phosphates were 2.4 ppm and amount of sulphates were 200 mg/Kg.

XRD data was given in Table-4 (Fig. 3). The data shows the presence of SiO_2 and muscovite mineral $[KAl_2(AlSi_3O_{10})(F,OH)_2]$.

TABLE-4
X-RAY DIFFRACTION ANALYSIS OF SOIL SAMPLE

Peak no.	2θ (°)	d-Spacing
1	8.969	9.85171
2	12.644	6.99529
3	17.851	4.96500
4	20.957	4.23555
5	26.688	3.33753
6	28.088	3.17427
7	29.970	2.97916
8	36.620	2.45196
9	39.507	2.27915
10	42.526	2.12408
11	50.183	1.81648

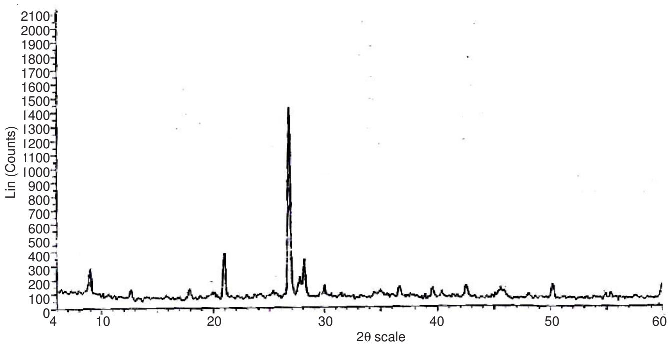

Fig. 3. XRD graph for analysis of soil

Conclusion

From the above results it was concluded that Langmuir isotherm is a better model to describe the adsorption of Ni, Cu and Co. Adsorption of Cd and Pb and Cr follows Freundlich isotherm. From the % age removal data, it was concluded that adsorption of relevant metals are in order of Ni > Co > Pb > Cu > Cr > Cd.

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