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Studies on The Removal of Hexavalent Chromium From Synthetic Waste Water By Using Activated Biocarbon

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ABSTRACT

The adsorption of chromium ions from an aqueous solution with galinsoga parviflora (GS) was studied in a batch set up as a function of contact time, pH, Chromium ion concentration and adsorbent dosage. The Langmuir and Freundlich adsorption models were applied to describe the isotherms and isotherm constants. The adsorption data gave a right fit with Langmuir isotherms with maximum adsorption capacity of 97 % of chromium (VI) ion. The outcomes depict the full potentiality of using galinsoga parviflora as an adsorbent for removal of Cr (VI) from aqueous solutions.

Keywords: galinsoga parviflora(GS), adsorbent, zinc chloride, contact time, metal adsorption, adsorption isotherm.

INTRODUCTION

Chromium as one of the major pollutants of the environment is available in nature as an odorless, hard metallic element. It is the seventh most abundant elements on the earth. Chromium exists as stable hexavalent and trivalent forms. The hexavalent chromium is more toxic than trivalent chromium and is often present in waste water as CrO_4^{2-} and $Cr2O_7^{2-}$.This is of serious environmental concern as Cr (VI) persists indefinitely in the environment complicating its removal. The hexavalent chromium has been considered more hazardous to public health due to its mutagenic and carcinogenic properties. Chromium can be released to the environment through a large number of industrial operations, including metal finishing industry, iron and steel industries and inorganic chemicals production (Gao et al., 2007). The adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost. The adsorption, with the selection of suitable adsorbents, can be an effective technique for the removal of heavy metals from waste water [1] - [4], [6], [8]. Some of suggested adsorbents are mesquite tree [9], biosorbents [5], [7], [10], agricultural biomass [11].

MATERIALS AND METHODS

Metal solutions
All the reagents were of analytical reagent grade were prepared in double distilled water. An aqueous stock solution (1000mg/l) of Cr (VI) ions was prepared using potassium dichromate ($K_2Cr_2O_7$). This was used as the source of Cr (VI) in the synthetic waste water.

Preparation of adsorbent
Galinsoga parviflora (mookthipoo-tamilname) was collected from local environment of Neman village, Thanjavur, (India,). The collected biomaterial is washed extensively in running tap water and with deionized water to remove dirt and particulate matter. The dried plant materials are powdered and activated in 2N zinc chloride solution. The activated biosorbent was carbonized and stored in desiccators and used for adsorption studies.

Adsorption studies
Adsorption experiments were carried out in batches 50 ml of 30 mg/l of Cr (VI) solution with 0.2g of activated carbon. The pH of the solution was kept at 2.6 for all experiments.The pH values of solutions were adjusted to dilute 0.1N HCl or NaOH solution by using pH meter. The temperature of experiments was maintained at 303K.The solutions were shaken in an orbital shaker (250rpm) for 160 minutes to study pH, carbon dosage and concentration and then filtered using filter paper and chromium concentration was measured using Hach Spectrophotomer DR5000.

To examine the effect of pH, adsorption experiments were conducted at different pH ranging from 2 to 8 at 30 mg/l of Cr (VI) solution. The optimum pH was determined from this study [12]. The adsorption studies were also conducted in batch experiments as a function of adsorbent dosage (0.1g to 0.2g) and metal ion concentrations (30, 40, 50 mg/l) for maximum adsorption.

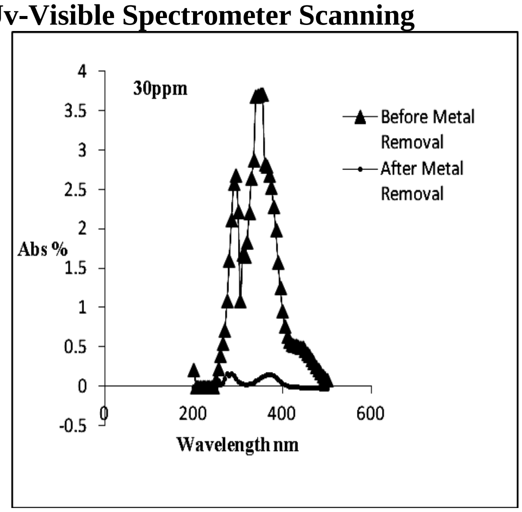
The percentage of Cr (VI) ions adsorption per unit mass of adsorbent (q_e in mg/g) was calculated by using the following expression:

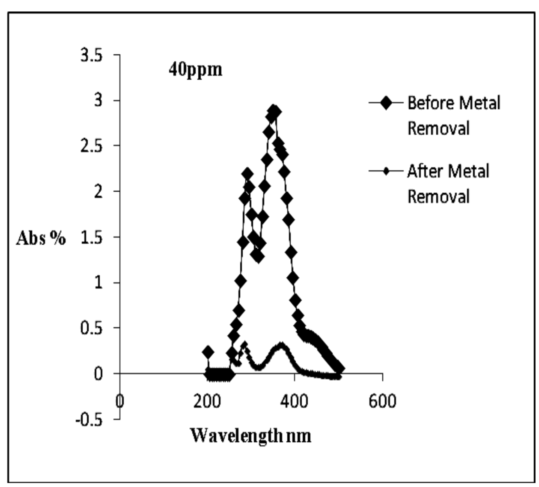
$$\% \text{ adsorption} = (C_i\text{-}C_e/C_i)*100$$

Where C_i and C_e are the initial and equilibrium concentration of Cr (VI) ions in solution.

RESULTS AND DISCUSSION

Uv-Visible Spectrometer Scanning





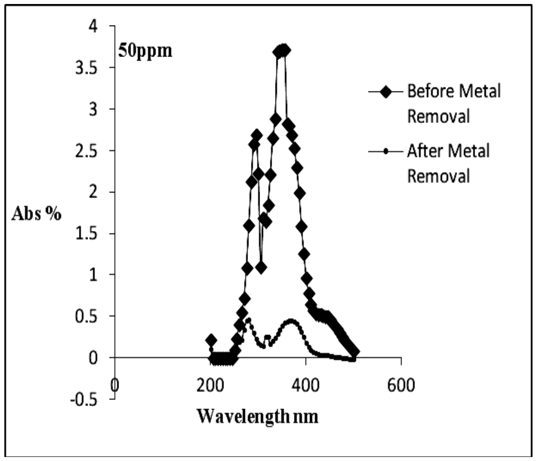


Fig1. Show UV-VIS Spectrophotometer Scanning Wavelength Vs Absorbance

The fig1 show the UV-VIS spectrophotometer 200 nm to 500 nm scanning result show the before and after metal adsorption.The absorbance of an aqueous solution of synthetic waste water shows maximum absorbance and after metal adsorption,the absorbance of the aqeous solution of synthetic waste water shows minimum. This indicates that Cr (VI) metal adsorbed by acivtated carbon from synthetic waste water. This confirmed the removal of Cr (VI) ion from the synthetic waste water.

Effect of pH

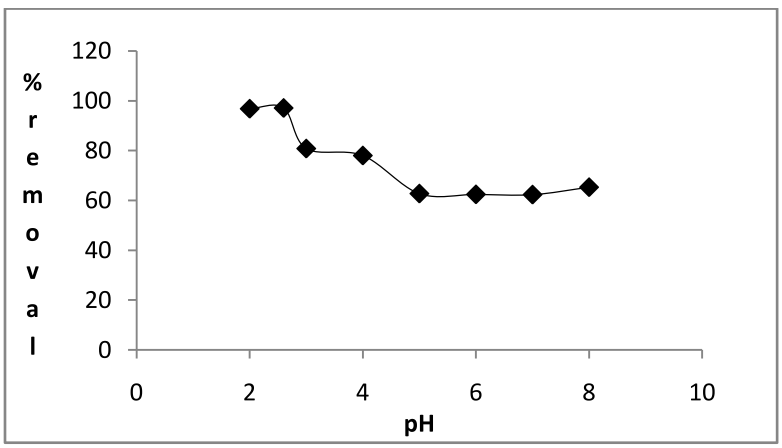


Fig 2. Effect of pH on the adsorption of Cr(VI) ions(initial concentration=30mg/l, temperature=303K,contact time=160min and adsorbent dosage 0.2g/l)

The P^H of solution is the most important parameter affecting metal ion adsorption. This is because the hydrogen ion competing with the positively charged metal ions on the active sites of the adsorbent [13]. The effect of pH on adsorption of Cr (VI) ions on to (GS) has been studied by varying it in ranges from 2 to 8 as shown in fig (2). As shown in fig (2), the uptake of Cr (VI) ions depends on pH, the maximum at pH 2.6 and then declining at higher pH.

Effect of adsorbent dose

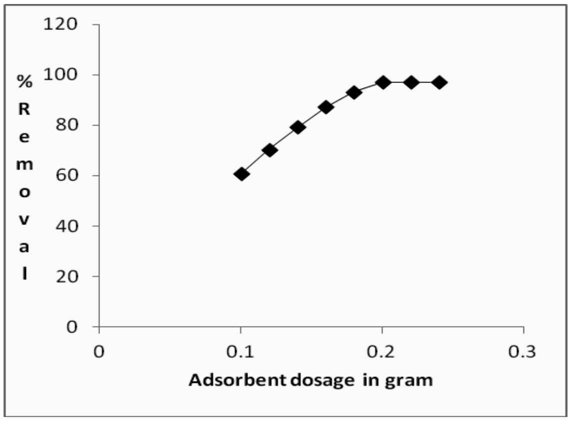


Fig 3. Effect of adsorbent dosage on the adsorption of Cr(VI) ions(initial concentration=50mg/l, temperature=303K, contact time=90min and pH 5.0)

Adsorbent dose is an important parameter that strongly influences the adsorption process by affecting adsorption capacity of the adsorbent. [14] The adsorption studies of Cr(VI) ions on to (GS) were done at 303K temperature by varying the quantity of adsorbent from 0.1g to 0.2g while keeping the volume of the metal solution constant at pH 2.6.The influence of adsorbent dose in percent adsorption of Cr(VI) ions is shown in fig(3).The results from fig (3) indicates that the adsorption increased with increase in the dose of the adsorbent .The increase in the adsorption percentage is due to the increase in active sites on the adsorbent and thus making easier penetration of the metal ions to the adsorption sites.

Effect of contact time

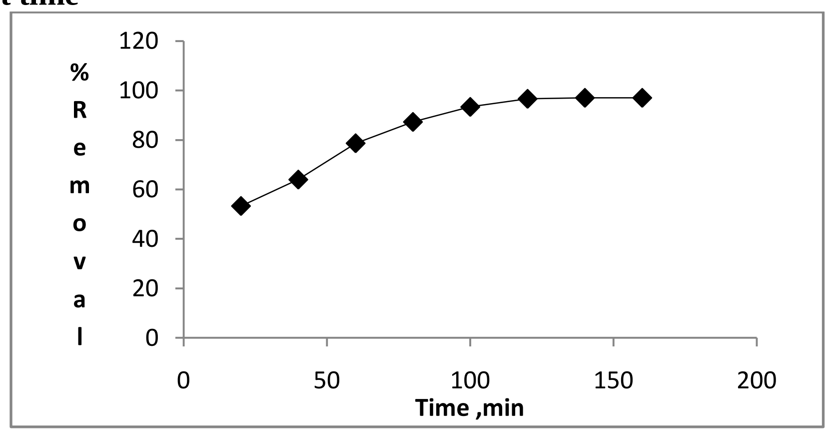


Fig 4. Effect of time on the adsorption of Cr (VI) ions (initial concentration=30mg/l, temperature=303K, pH 2.6 and adsorbent dosage 0.2g/l)

Batch adsorption experiments were carried out by 0.2g of the adsorbent(GS) with 50 ml of chromium ion solution in a series of flask were taken and kept in orbital shaker and Shaking time was varied from 30 to 160 min. As can be seen in fig 4, the percentage removal of ion increased with the time of shaking .A sharp increase was observed at around the time of 140 min (97 % removal) and attained an optimum at the time of 160 min. Hence the contact time 160 minutes was set for all the other experiments. The equilibrium time is one of the important parameters for an economical wastewater treatment system. In contrast 98.5% removal was achieved at 150 min in studies on biosorption of Cr (VI) from aqueous solutions using indigenous materials [15].

Adsorption isotherm

Adsorption isotherms describe how adsorbate interacts with adsorbents and therefore are critical in optimizing the use of adsorbents. In order to optimize the design of an adsorption system. It is essential to establish the most appropriate correlation for the equilibrium curve. Several isotherm equations are available for analyzing experimental data and the important isotherms were selected in this study.

Langmuir Isotherm:

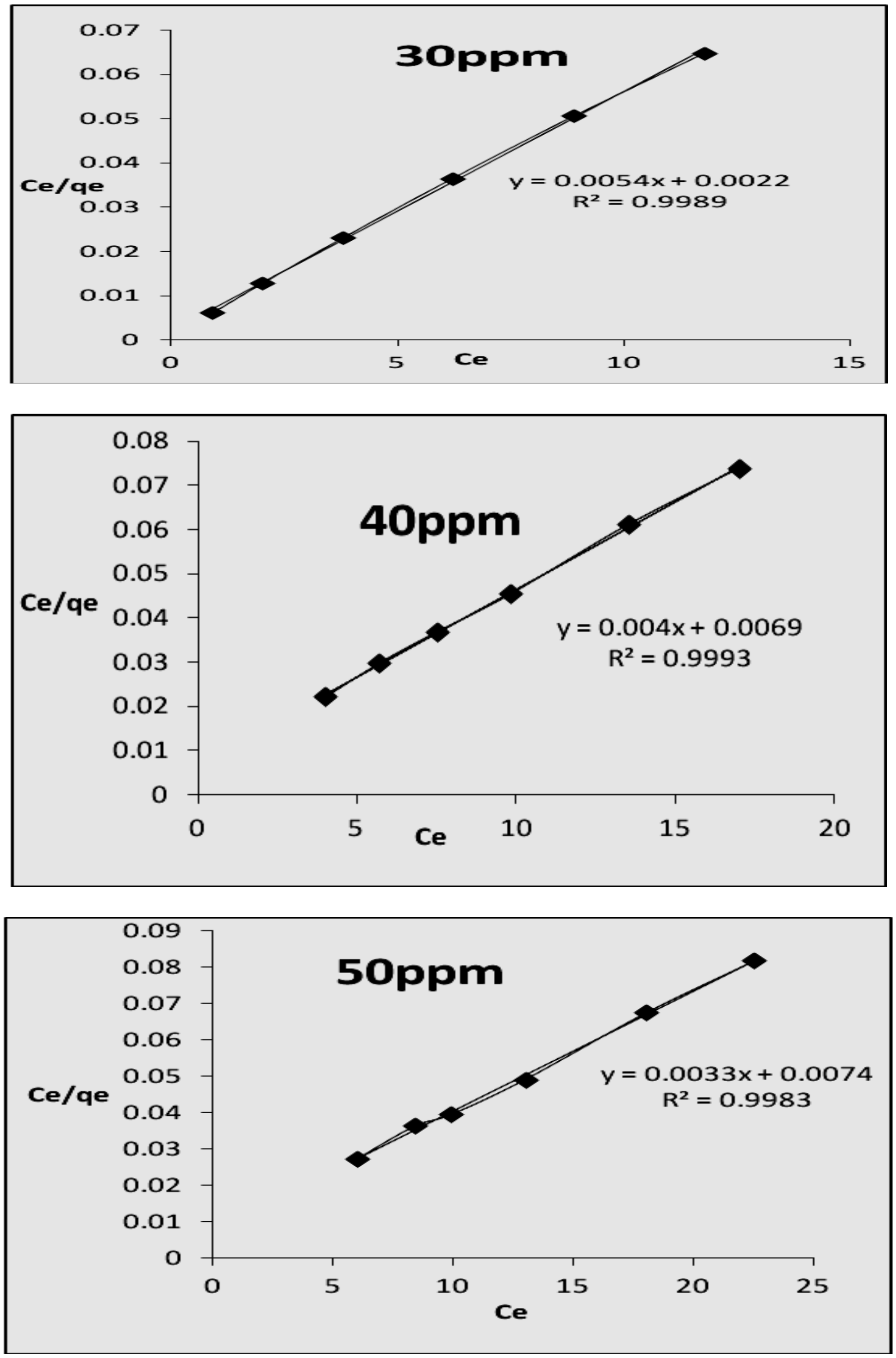


Fig 5. Langmuir adsorption isotherm plot for the adsorption of Cr(VI) ions at 303 K

This model assumes that the adsorptions occur at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption processes [16].The data of the equilibrium studies for adsorption of Cr (VI) ions onto (GS) was followed by the following forms of Langmuir model:

$$C_e/q_e = (1/Q_o)* c_e + 1/b\ Q_o$$

Where C_e is the equilibrium concentration(mg/dm3); q_e is the amount of Cr(VI) ions adsorbed at equilibrium (mg/g); Q_0 and b are Langmuir constants related to adsorption capacity (mg/g) and energy of adsorption (dm3/mg) which reflects quantitatively the affinity between the adsorbate and adsorbent. The values of Q_o and b can be obtained from the slope and intercept of the plot of C_e/q_e against C_e respectively as can be seen in the figs (5). The high value of correlation coefficient R^2 from table 1 indicates that the adsorption of Cr (VI) ion to (GS) was followed by the Langmuir isotherm model. The table 1 also gives information about the adsorption capacity (Q_0) and energy of adsorption b on to (GS).

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L which is defined by

$$R_L=1/(1+bC_0)$$

Where b is the Langmuir isotherm constant and C_0 is the initial Cr (VI) concentrations. R_L value indicates the type of the isotherm. The adsorption process as a function of R_L may be described as [12]

$R_L > 1$ Unfavourable

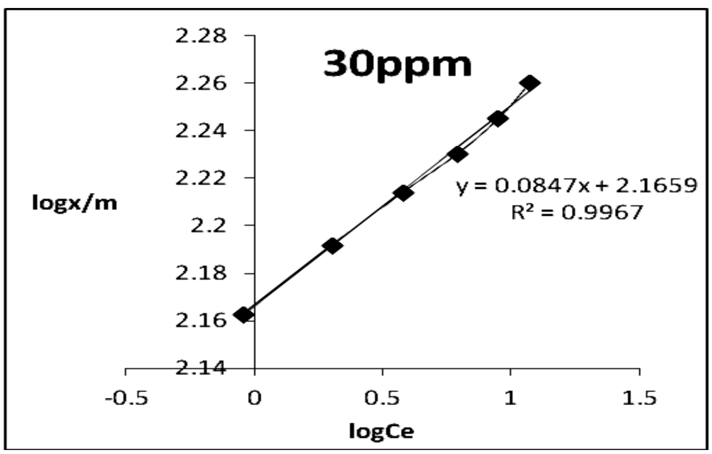
$R_L = 1$ Linear

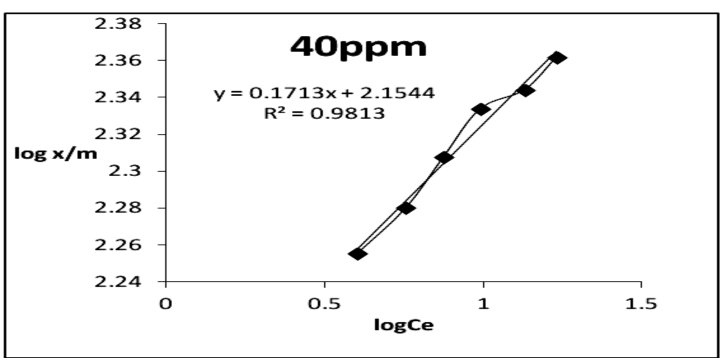
$O < R_L < 1$ Favourable

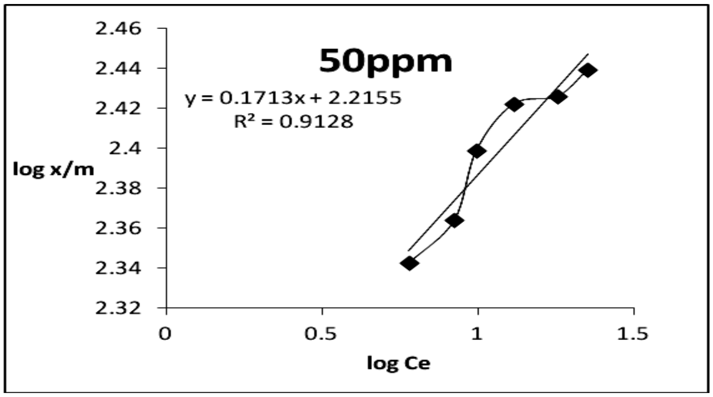
$R_L = 0$ Irreversible

In the present study, the calculated R_L value for adsorption of Cr (VI) ion on to (GS) obtained at 303 k based on Langmuir isotherm for the adsorption of Cr (VI) ion onto (GS) was found to be $0 < R_L < 1$ and this indicates a highly favourable adsorption within the concentration range 30,40,50 mg/l [17]

Freundlich Model







Figs 6. Freundlich adsorption isotherm plot for the adsorption of Cr(VI) ions at 303 K

The Freundlich model can be applied for non-ideal sorption on heterogeneous surfaces and multilayer adsorption [18].It is expressed by the following equation

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

The equation linearized by taking logarithms

$$\mathrm{Log}\,(q_e) = 1/n \log C_e + \log K_f$$

The Freundlich intensity of adsorption (1/n) and adsorption capacity K_f were calculated from the slope and intercept of the plot of log(q_e) against log(C_e) respectively which are shown in figs 6. The high value of correlation coefficient R^2 from table 2 indicates that the adsorption of Cr (VI) ion to (GS) was followed by the Freundlich isotherm model. The table 2 also gives information about the adsorption capacity K_f and intensity of adsorption (1/n) on to (GS).

Table 1 Langmuir adsorption isotherm parameters and correlation coefficients for adsorption of Cr (VI) ions on to(GS) at 303 K.

Langmuir Parameters			
Ppm	30	40	50
Q_o	185.19	250.00	303.03
B	2.45	0.58	0.45
R^2	0.9989	0.9993	0.9983

Table 2 Freundlich adsorption isotherm parameters and correlation coefficients for adsorption of Cr(VI) ions on to (GS) at 303 K.

Freundlich Parameters			
Ppm	30	40	50
N	11.80	5.84	5.84
K_F	146.52	142.69	164.25
R^2	0.9967	0.9813	0.9128

SEM(Scanning Electron Microscope)

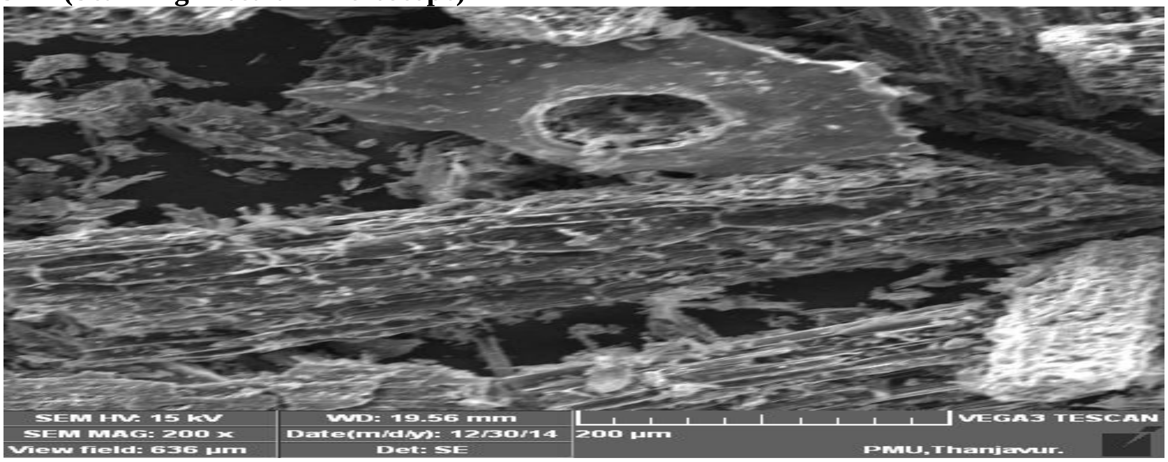


Fig 7. Images of adsorbent before metal adsorption

There are many active sites at the surface available for adsorption for adsorbent as shown in the fig 7. It is evident that the adsorption sites are readily to allow the adsorbate.

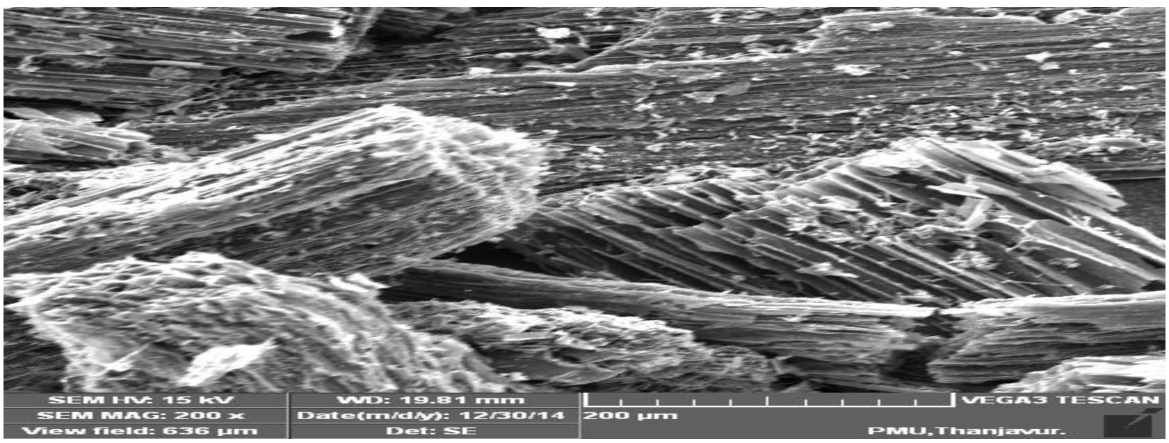


Fig 8. Images of adsorbent after metal adsorption

Fig 8 shows the SEM micrographs of the metal adsorption. It is clear that the adsorbent has considerable numbers of heterogeneous layer of pores where there is a good possibility for the chromium ion to be adsorbed. The surface of metal –loaded adsorbent, however, clearly shows that the surface of the adsorbent is covered with metal

XRF spectrum

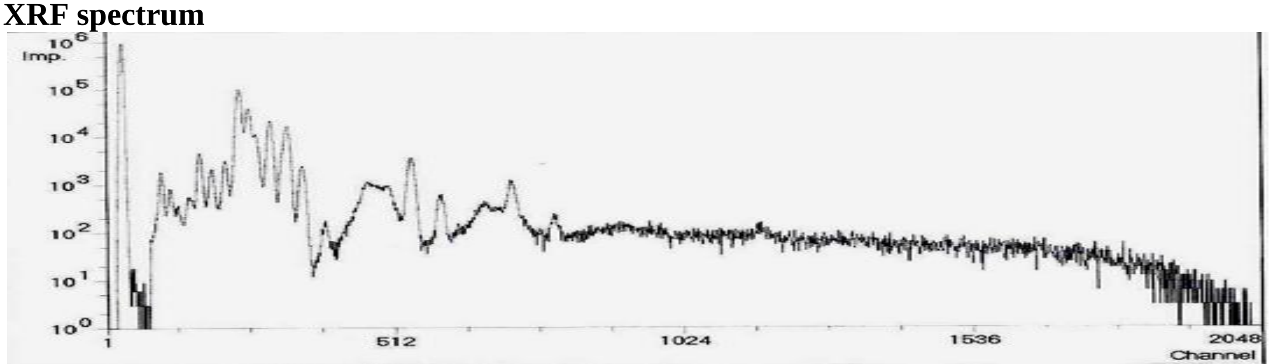


Fig 9. XRF spectrum of adsorbent before metal adsorption

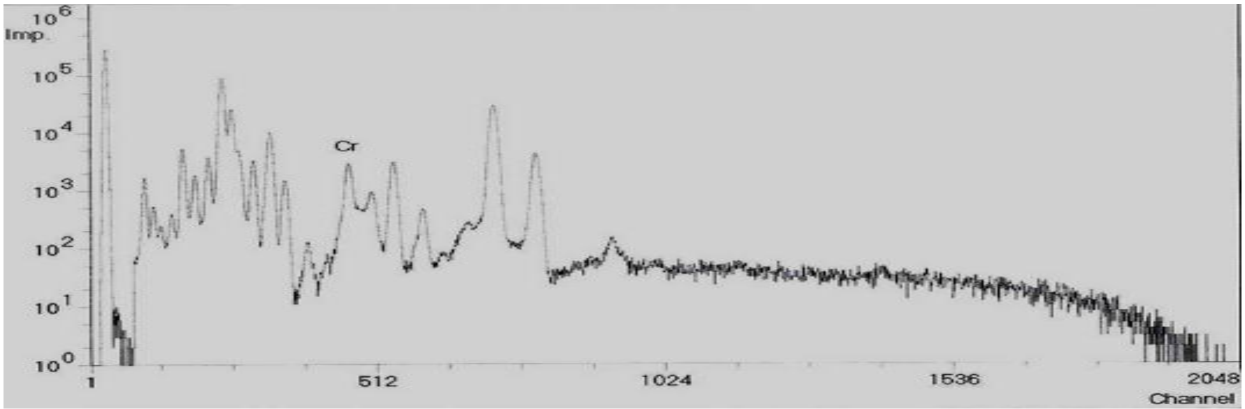


Fig 10. XRF spectrum of adsorbent after metal adsorption

Fig 8 and Fig 9 show the XRF spectrum of before metal before and after metal adsorption of adsorbent. Fig 9 shows XRF spectrum of adsorbent consist of chromium peak of 462- channel, energy- 5.425,counts -2853 .This confirmed the removal of Cr(VI) ion from the synthetic waste effluent water.

CONCLUSIONS

This work clearly indicates the potential of using activated carbon as an excellent adsorbent for the removal of Cr (VI) ions from aqueous solutions. The optimum pH was found at pH 2.6 for the removal of Cr (VI) ions on to (GS). With increasing the adsorbent dosage, the adsorption percentage also increases. The equilibrium data were analyzed for the Langmuir and Freundlich isotherm model. Among these, Langmuir isotherm fitted well with the experimental data than Freundlich isotherm. The result of investigations is quite useful in developing an appropriate technology for designing a waste water treatment plant for the removal of Cr (VI).

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