TECHNIQUES FOR THE REMOVAL OF METAL COMPLEXES FROM INDUSTRIAL EFFLUENTS.

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ABSTRACT

The Industrial effluents in mysuru and nanjangodu were collected from Jubilant, Zenith textiles, AT & S and KSIC (Silk factory). The effluents were analyzed for metals complexes. In all the effluents, the metals like Copper, Zinc, Chromium and Lead were common with different concentrations. The metals were made to react with the reagents (ligands) to form metal complexes using the respective reagents. The known amounts of adsorbents like Egg shell, Chewing tobacco and Garlic husks were added and removed the metal complexes from the industrial effluents. The Calcium and Magnesium were determined and from the tap water. The parameters like, effect of pH, dose and time were studied. The adsorbents were analysed by XRD. Before and after adsorption, the adsorbents were characterized. The adsorption isotherms were also studied.

Key Words: *Hard water, Industrial effluents, Adsorbents, Metal complexes, XRD.*

No:of Tables: 4 **No: of Figures : 15** **No: of References: 12**

INTRODUCTION

Heavy metals are toxic even at very low concentrations and pose serious problems due to their possible entry into the food chain [1]. Heavy metals contamination in the environment potential hazards to human health. All the metals are naturally capable of accumulation in soil as well as in water eco-systems. It is difficult to eliminate the metals which are persistent contaminants, once added to the environment. They often accumulate in the tissues of the organisms & cannot be excreted. Removal of toxic heavy metals from industrial waste water has been practiced for several decades, the conventional physico-chemical removal methods such as chemical precipitation, electroplating, membrane separation, evaporation or resin ionic exchange are usually expensive and sometimes not effective. Therefore, there is a need for some alternative techniques, which should be efficient and cost effective [2].

In an increasing search for low cost adsorbents, various substances like, Egg shell [3], Coconut charcoal [4], Tamarind kernel powder [5], Ricinus communis [6], Agaricus bisporus [7], Rice husk [8], Gingelly oil cake [9] etc.

In the present study we have investigated the removal of metals from the industrial effluents in the form of complexes using natural adsorbents like Garlic husk, Chewing tobacco and Egg shell as adsorbents. The metals which are found in the effluents are Copper (II), Zinc (II), Lead (II) and Chromium (III). The Calcium and Magnesium are removed from the hard water (tap water). The parameters like effect of pH, dose and time were studied with the maximum adsorption of metal complexes.. The rate kinetics and adsorption isotherms indicate that all the three adsorbents are very good adsorbents.

Materials and methods

Processing of Egg shells as adsorbents

Egg was boiled and peeled off for its shell and air or sun dried to dryness. Then, it was heated in hot air oven for 1½ to 2 hrs until shell gives pungent smell at 150^0 C. The egg shell was treated with 2N HCl solution. Then, it was washed with water and once again kept in hot air oven for dryness 150^o C. After half an hour, it was removed from hot air oven and crushed manually with pestle and mortar to increase the surface area.

Processing of Chewing tobacco as an adsorbent : Chewing tobacco was brought from local shop and was sieved for the leafy particles. Then, it was treated with 2N hydrochloric acid for one hour, washed with water to remove HCl and treated with 2 % sodium hydroxide for one hour. Once again, was washed with water. pH was maintained at neutral condition by adding hydrochloric acid. Then, treated tobacco was sun dried for two days, preserved in plastic container.

Processing of Garlic husk as an adsorbent.Freely available garlic husk was cleaned, kept in hot air oven for 30-45 minutes at 150^0 C and was treated with 2N HCl, for acid activation, washed thoroughly with distilled water, squeezed and then once again kept in a hot air oven, maintained at 150^oC. Using the mixer, it was powdered and then used for adsorption process.

Collection of effluent sample and detection of metals:

The industrial effluents were collected from four industries namely Jubilant (sample-1), Zenith textiles (sample-2), AT & S (sample-3) and KSIC [(Silk factory) (sample-4)]. The effluents were analysed for the determination and estimation of heavy metals shown in TABLE-1.

TABLE-1 : Concentrations of metals present in different industrial effluents.

Metals in Industrial effluent	AT & S in un treated effluent	Jubilant	Silk factory	Zenith
Copper (mg/L)	986	0.20	ND*	0.05
Zinc (mg/L)	0.18	0.20	0.16	0.13
Lead (mg/L)	0.02	ND	0.01	ND
Chromium (mg/L)	0.30	0.3	0.25	0.1

*ND-Not detectable.

Preparation of metal complex solutions

Preparation of Copper complex:

The dithizone (0.2%) was added to the industrial effluent to precipitate out the Lead. The filtrate with Copper was taken, and 0.2 % of Zincon was added. The blue color of Copper-Zincon complex was formed and solution was used for adsorption studies.

Preparation of Zinc complex:

For 100 ml of industrial effluent, 2 ml of buffer solution of pH 10 and a pinch of Eriochrome black-T were added to give wine red color. EDTA (1%) of 20 ml was added to give blue colored Zinc- EDTA complex. This solution was used for adsorption studies.

Preparation of Lead complex:

100 ml of industrial effluent was taken in conical flask, to which nitric acid (1ml) was added. Then 2 % solid hexamine of 10 ml, EDTA (1%) of 10 ml was added to give yellow color of Lead complex. This solution was used for adsorption studies.

Preparation of Chromium complex:

0.25 % of 1, 5- diphenyl carbazide (50 ml), 5 ml of Sulphuric acid were added to industrial effluent to give complex of chromium & diphenylcarbazide. Then, this solution was used for adsorption studies.

Preparation of Calcium and Magnesium complexes:

The hard water (100 ml) was collected to which two or three total hardness tablets were powdered and added, to give wine red color on adding EDTA (0.372 g). The fuel solution becomes blue and was used for the adsorption study of Calcium and Magnesium by diluting to required concentrations.

Adsorption isotherms:

In order to determine the sorption potential of adsorbent, the study of sorption isotherm was essential in selecting an adsorbent for the removal of the metal complex. The adsorption data was studied with the Freundlich and Langmuir's isotherms [10].

Freundlich isotherm: $\log q_e = \log K + (1/n \log C_e)$

Langmuir isotherm: $C_e/q_e = (1/Q_o b) + (C_e/Q_0)$

where, q_e - amount of metal complex adsorbed per unit mass of adsorbent (mg/g) at equilibrium, K and n are respectively, the measures of sorption capacity and intensity of adsorption, C_e equilibrium concentration of metals (in mg/L), Q_o and 'b are the Langmuir's constants, indicating the sorption capacity (in mg/g) and energy of adsorption (in g/L) respectively from the slope and intercept.

Kinetics of adsorption

The following equation proposed by Kannan and Vanamudi 1991 [11] was employed for adsorption data to find the order of the reaction:

$$k_1 = (2.303/t) \log (C_o/C_t),$$

where, C_o and C_t are concentrations of metals at zero and time t (min). The values of $\log (C_o/C_t)$ were found to be linearly correlated with the contact time for different metals.

Further, the essential characteristics of the Langmuir isotherms can be described in terms of a dimensionless constant, namely separation factor or equilibrium parameter, R_L which was defined by the equation, $R_L = 1/(1+bc_i)$ **[12],** where, b is the Langmuir's constant and C_i is the initial concentration of metals (in ppm). The value of the parameter, R_L indicates the nature of the isotherm as given below:

Table-2, R_L Value indicating the nature of isotherms

R_L value	Nature of Isotherm
$R_L > 1$	Unfavorable
$0 < R_L < 1$	Linear
$R_L = 1$	Favorable
$R_L = 0$	Irreversible

Experimental section:

Batch experiment

Metals complexes or dyes adsorption experiments were conducted in batch mode with 50 ml stock solution. The variables studied were adsorbent dose, pH and contact time. The mixtures were observed for adsorption process, after keeping the solutions for adsorption to take place.

- 1-5 grams of dose of adsorbents were added and kept for observation.
- The concentrations present in Industrial effluents were diluted to required (20-100 ppm) concentrations. 2 grams of

adsorbent was added and adsorption studies were carried out.

- One gram of adsorbent was added to the known concentration (10 ppm) of solution and readings were noted constantly for each hour.
- Five number of 50 ml samples of dye solutions (2-5 %) and varying dose of adsorbents (1-4 g) were added in series. Then, the solutions were kept for adsorption to take place.

RESULTS AND DISCUSSION

The effect of parameters like pH, dose of adsorbent and contact time on the removal of metals from industrial effluents was investigated with respect to natural adsorbents.

Effect of pH:

The metal complexes with the reagents either in acidic or basic medium were studied. The pH maintained was as follows:

- The Copper complexes with Zincon reagent without altering the pH in aqueous medium itself.
- The Zinc complexes with EDTA reagent in the basic condition.
- The Lead complexes with Hexamine reagent in acidic medium.
- The Chromium complexes with 1, 5-diphenyl carbozide reagent in acidic medium.
- The Calcium and Magnesium complexes with EDTA reagent in Basic medium.

Effect of dose:

The results show that, as dose increases, adsorption increases for all metal complexes (Fig-1).

Effect of concentration:

The results show that, as concentration increases, adsorption increases for all the metal complexes (Fig-2).

Effect of contact time:

The result shows that, as the time increases, adsorption increases (Fig-3).

Effect of dose Vs Concentration:

The results shown in Fig-4, indicate that, the dose and the concentration of all the dye solutions, for all the adsorbents are co-related to each other.

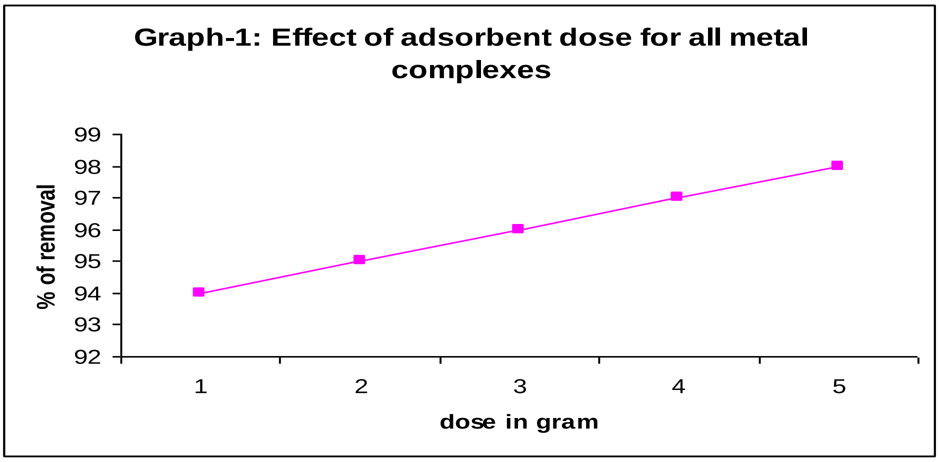


Fig-1, Graph showing effect of adsorbent dose for all metal complexes.

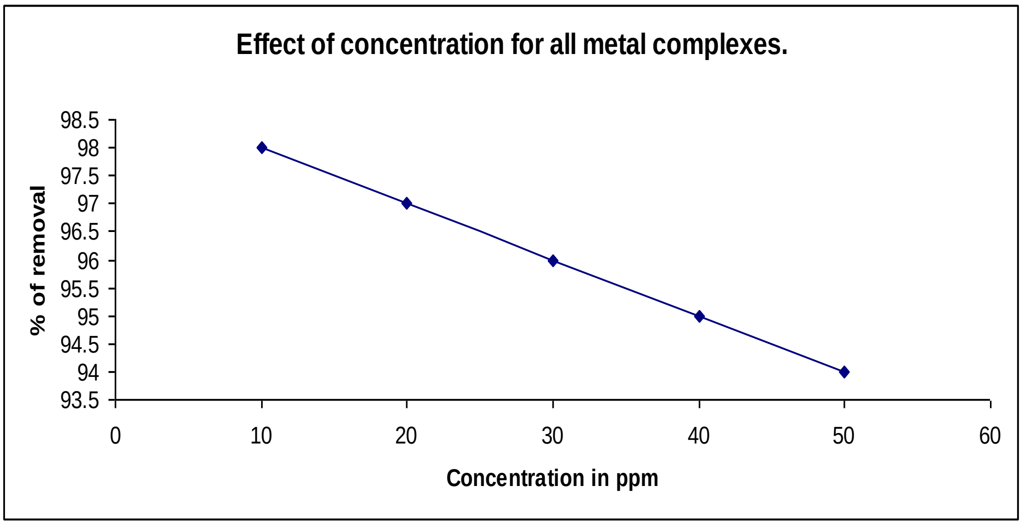


Fig-2, Graph showing effect of Concentration for all metal complexes.

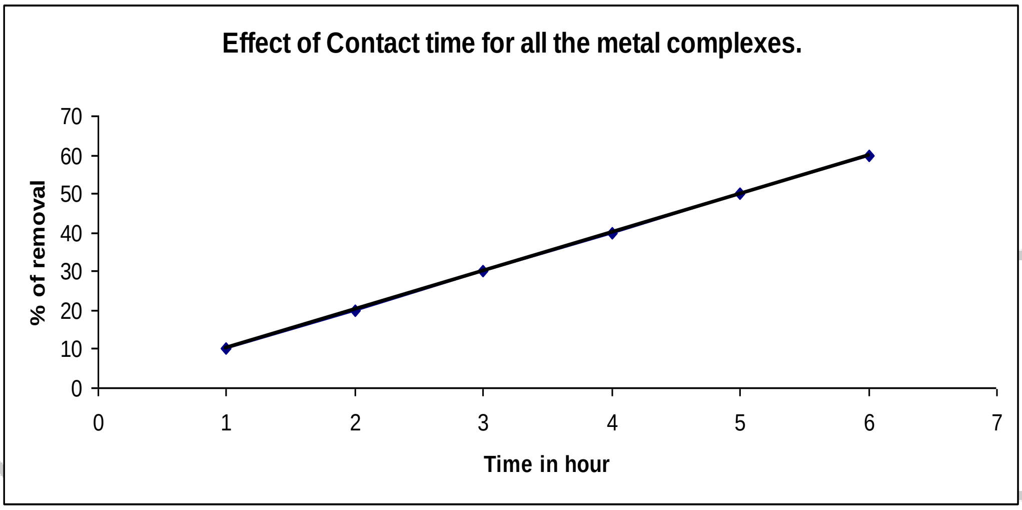


Fig-3, Graph showing effect of Contact time for all metal complexes.

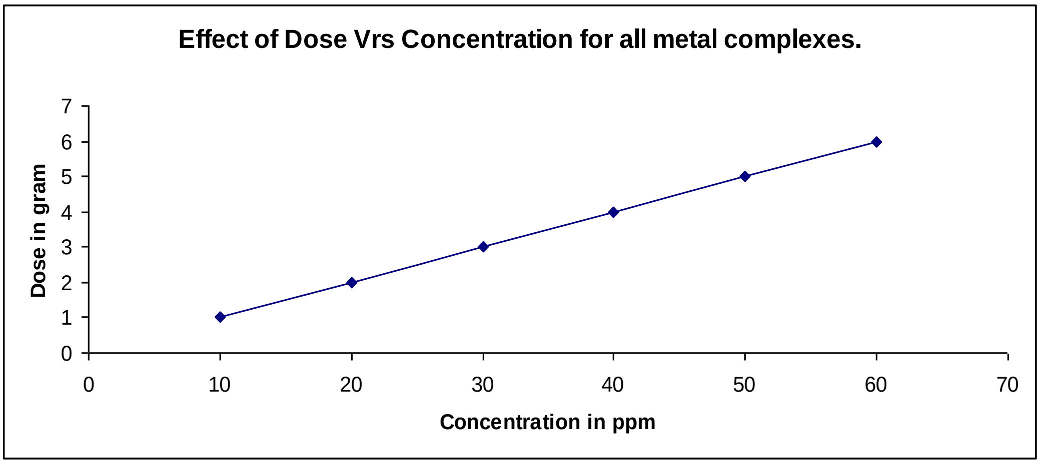


Fig-4, Graph showing effect of dose Vs Concentration for all metal complexes.

Table-4: Adsorption isotherms for removal of metal complexes/dyes from industrial effluents over Garlic husk, Chewing tobacco and Egg shell

Parameter	Garlic Husk	Chewing tobacco	Egg Shell
Freundlich isotherm:			
Slope(1/n)	**0.108**	**1.050**	**0.381**
Intercept(log k)	**0.143**	**0.175**	**0.216**
Correlation co-efficient (r)	**0.901**	**0.920**	**0.933**
Langmuir isotherm:			
Slope ($1/Q_o$)	**0.480**	**0.220**	**0.334**
Intercept	**0.525**	**2.00**	**3.100**
Correlation coefficient (r)	**0.986**	**0.972**	**0.934**
Kinetics of adsorption:			
10^2 k (min^{-1})	**0.052**	**0.059**	**0.030**
r-value	**0.982**	**0.974**	**0.975**

Photos indicating before and after adsorption of metal complexes from industrial effluents and tap water.

Fig-5, Chromium adsorption on Egg shell, Chewing tobacco and Garlic husk adsorbent:

Fig-6, Lead adsorption on Egg shell, Chewing tobacco and Garlic husk adsorbents:

Fig- 7, Copper adsorption on Egg shell, Chewing tobacco and Garlic husk adsorbents:

Fig-8, Zinc adsorption on Egg shell, Chewing tobacco and Garlic husk adsorbent:

Fig-9, Calcium and Magnesium (Tap water) adsorption on Egg shell, Chewing tobacco and Garlic husk adsorbents:

X-ray diffraction spectrum of adsorbents before and after adsorption.

Fig-10. XRD spectrum of Egg shell(adsorbent) before adsorption.

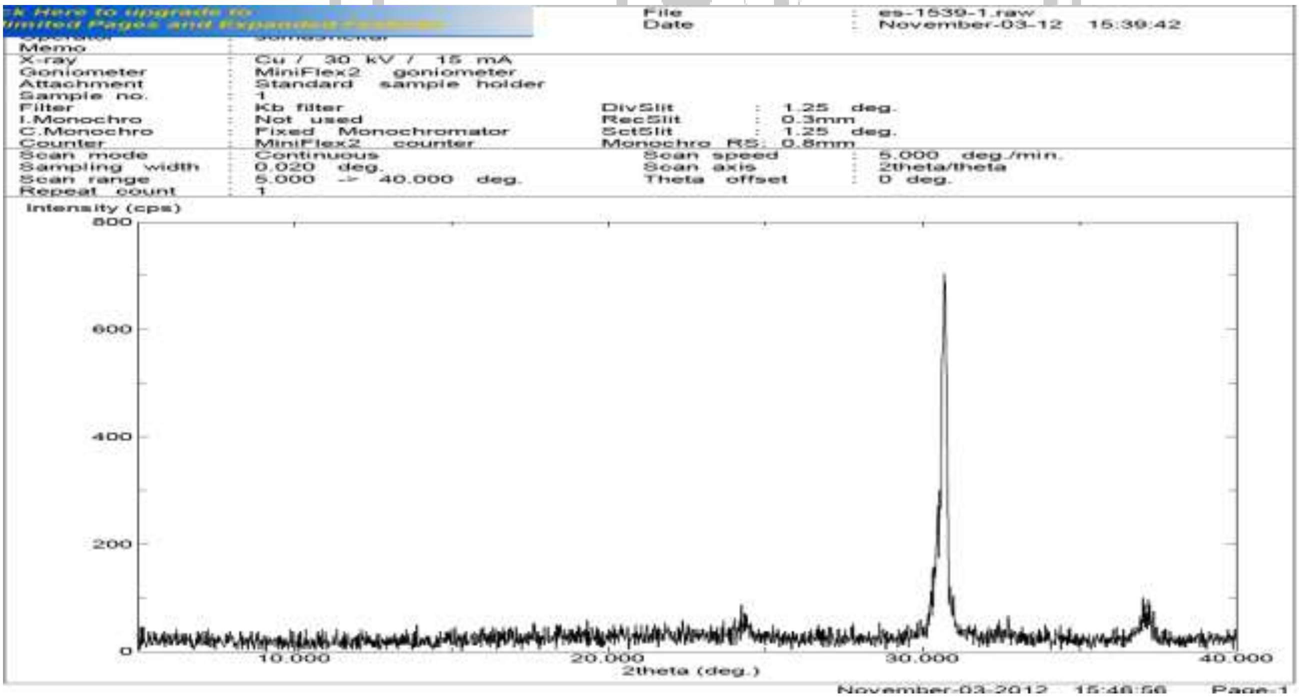


Fig-11. XRD spectrum of Egg shell after adsorption of Metal complex (Chromium complex with 1, 5-diphenyl carbazide)

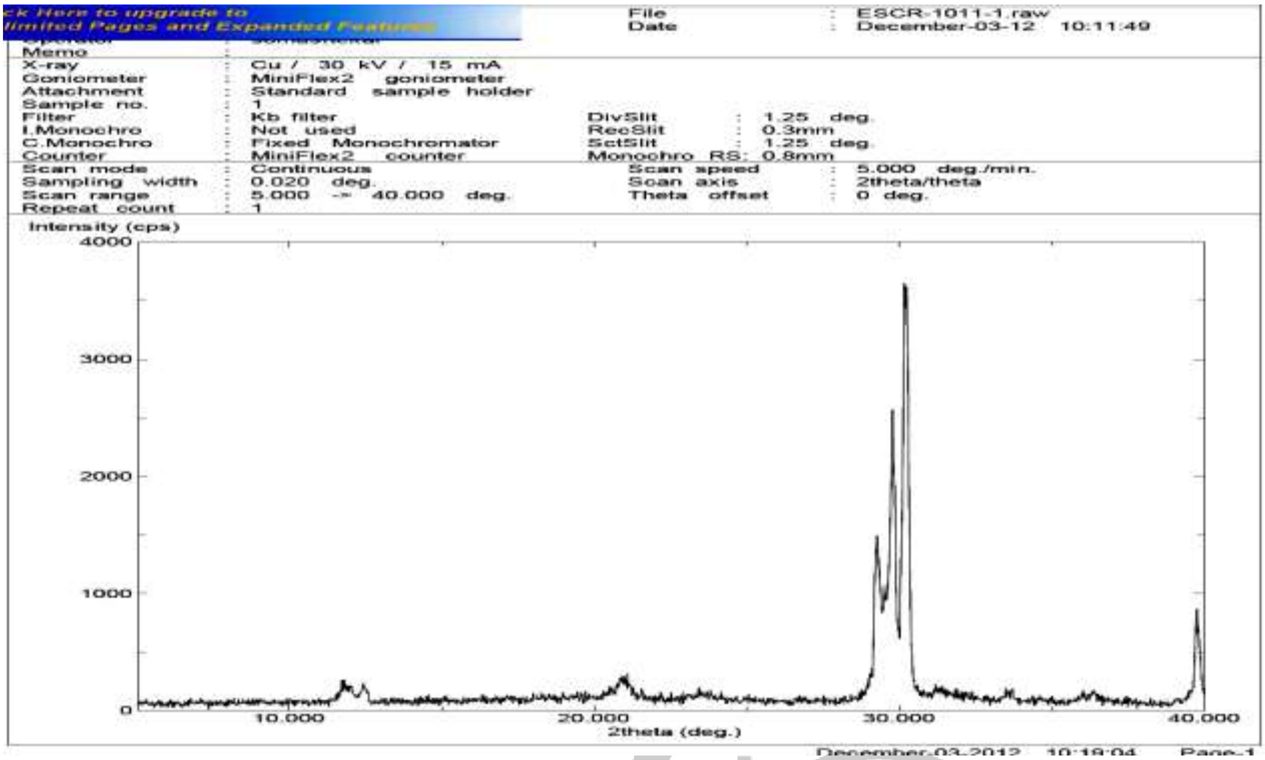


Fig-12, XRD spectrum of Chewing tobacco (adsorbent) before adsorption:

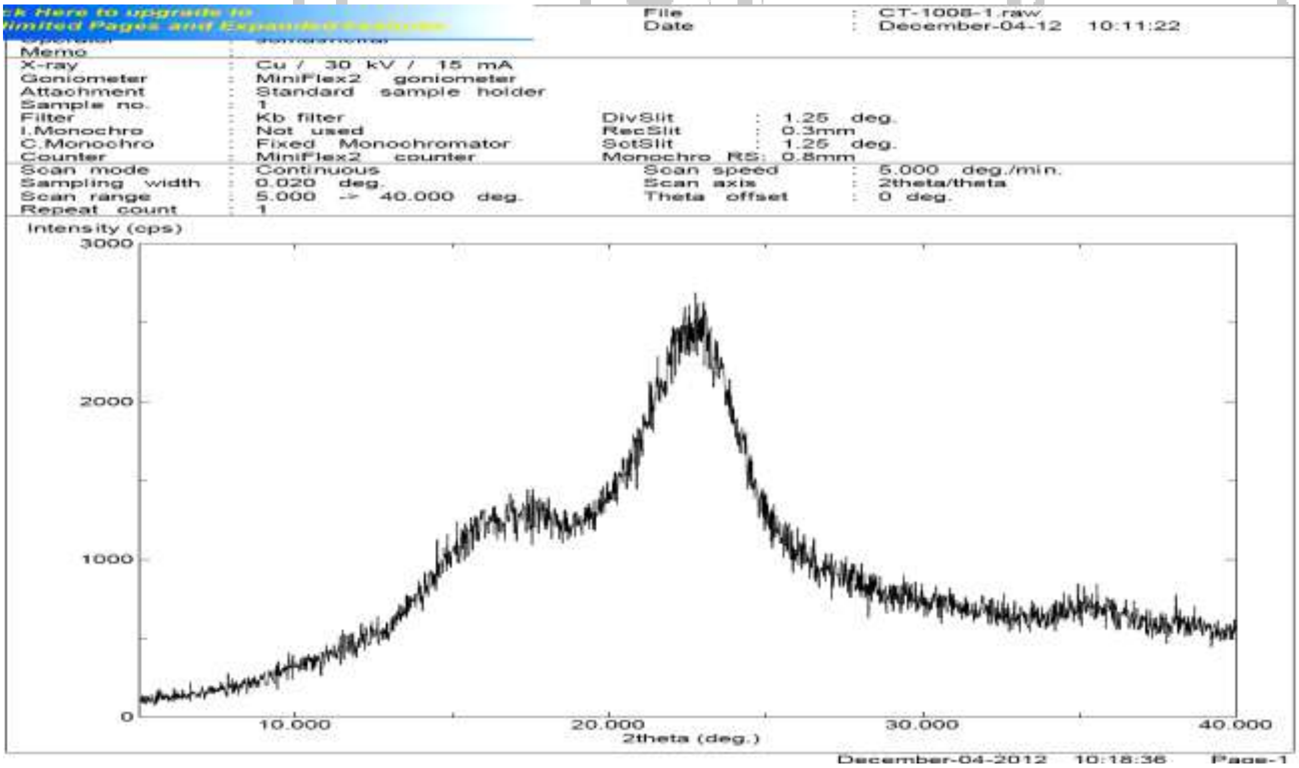


Fig-13.XRD spectrum of Chewing tobacco after adsorption of metal complex (Copper with Zincon).

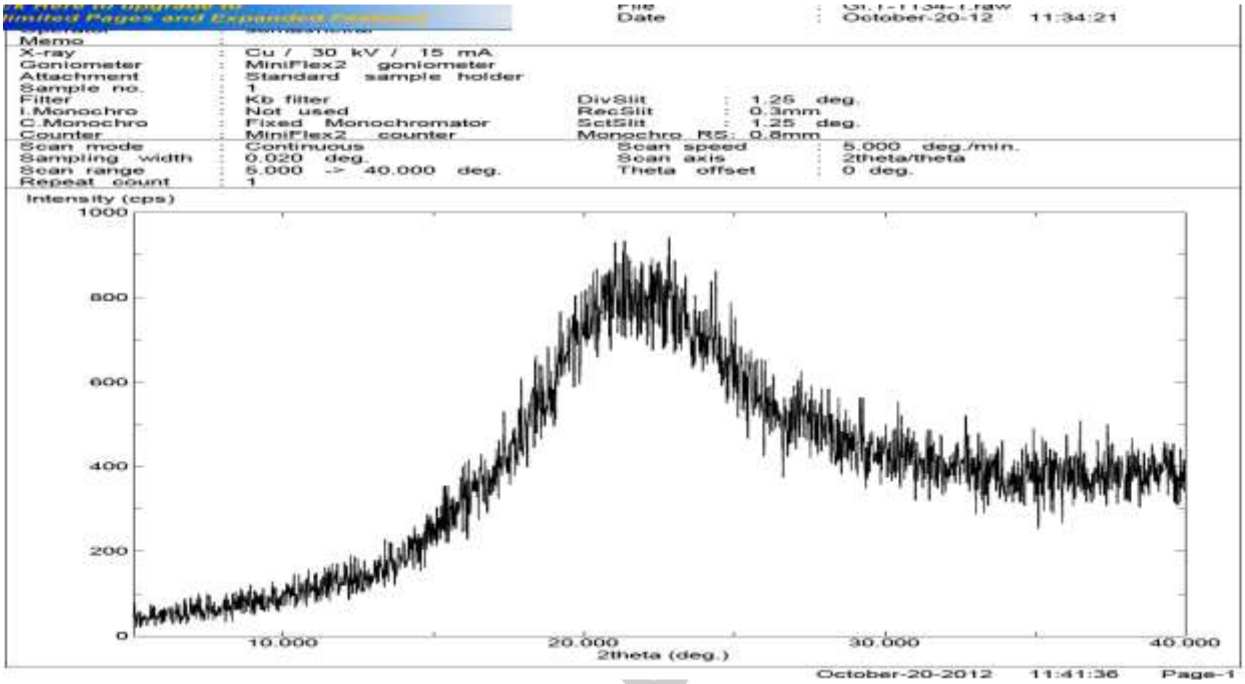


Fig-14.XRD spectrum of Garlic husk (adsorbent) before adsorption:

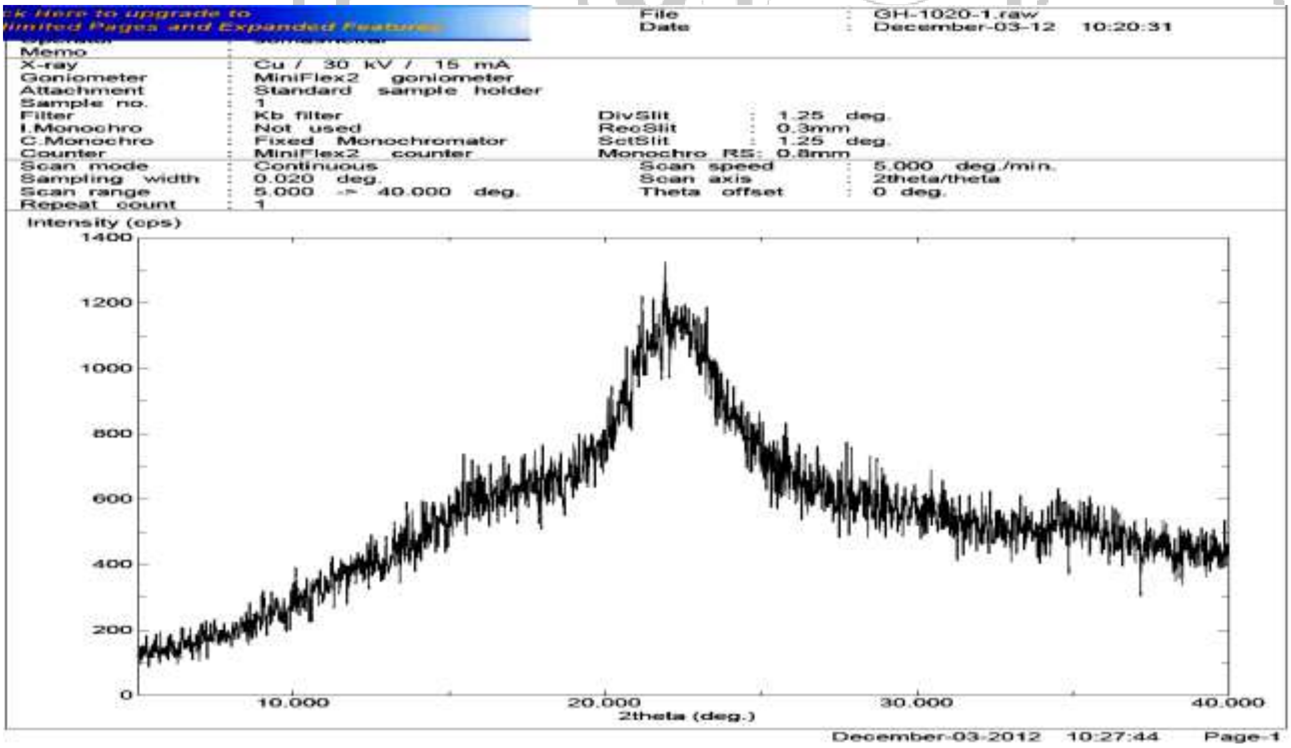
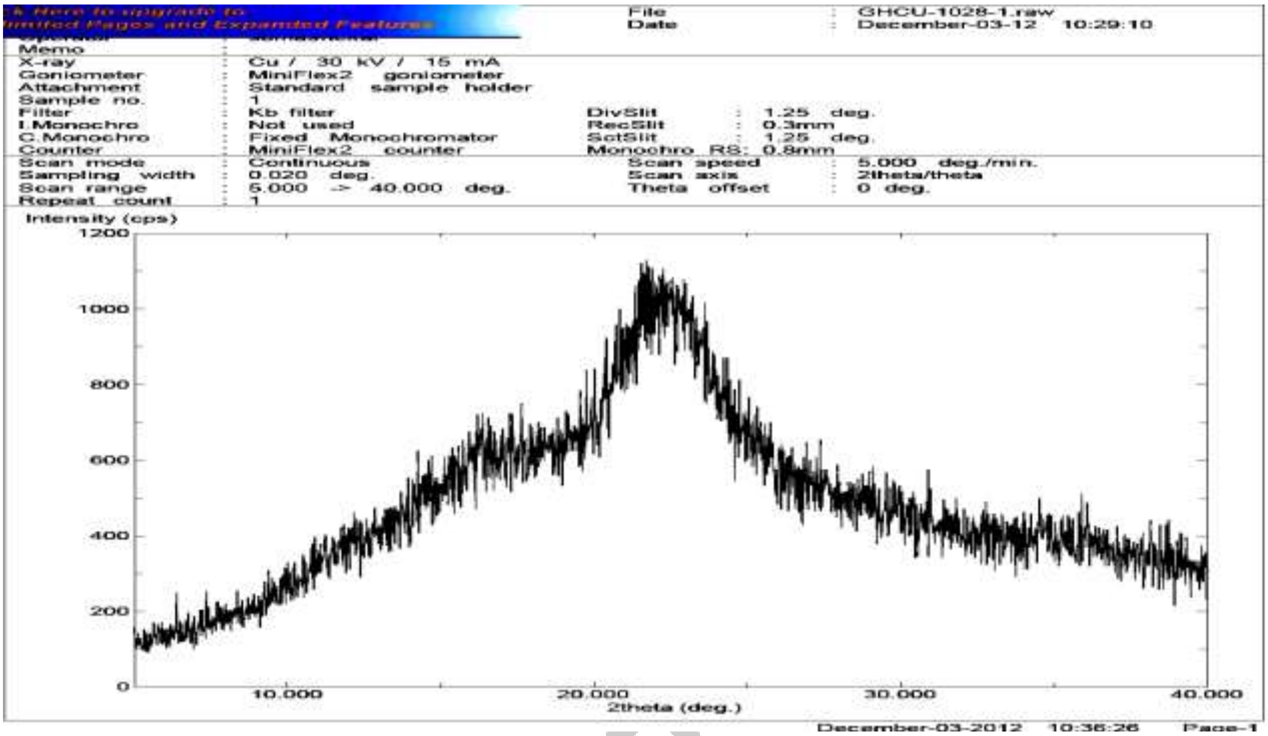


Fig-15. XRD spectrum of Garlic husk after adsorption of metal complex (Copper complex with Zincon):



Conclusion

The kinetic values [(10^2k min^{-1}) (0.052, 0.059 & 0.030)] for all the three adsorbents shows the model to be first order. R value lies within one which indicates the model developed is favorable. The models obey Freundlich and Langmuir isotherms and linear correlation between two variables. The XRD spectra show that, the intensity of the Egg shell without adsorption was 700 cps and after adsorption of metal complex the intensity was 3500 cps. For Chewing tobacco the intensity was 2500 cps, but after adsorption the intensity decreased to 900 cps. The intensity of Garlic husk shows 1300 cps, after adsorption the intensity decreases to 1100 cps which confirms the adsorption. The new adsorbents which have been developed are economically feasible compared to the other adsorbents and can be applied to industrial effluent treatment, for the metal removal.

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