

**TRIMETALLIC REMOVAL FROM WASTE WATER USING NOVEL MODIFIED BIOMATERIAL**

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**ABSTRACT**

The aim of the present study is to analyze the competitive biosorption of tri metallic combination [Cd (II), Cr (III) and Ni (II)] on modified *Ficus religiosa* leaves powder (FRLP) and compared with unmodified *Ficus religiosa* leaves powder. The adsorption capacities of the metal ions, when present in combination were tested on modified FRLP. These were found to be 10-30% higher as compared to unmodified *Ficus religiosa* leaves powder solutions and stability in terms of regeneration cycles [3 to 5]. Evidences in support of biomaterial designed have been provided on the basis of SEM, FTIR and TGA. Kinetic studies revealed that adsorption equilibrium in each case follows first order equation. Experimental findings indicate that FRLP has enough potential for the development of a simple, fast and eco-friendly method for decontamination of toxic metals from water bodies.

**Key words:** Biosorption, Regeneration, modification, decontamination, toxic metals, waste water

**INTRODUCTION**

Heavy metals can be distinguished from other toxic pollutants since their non-biodegradable nature and can accumulate in various ecosystems of environment. The main techniques which have been utilized to reduce the heavy metal ion content of effluents include lime precipitation, ion exchange, membrane processing, electrolytic methods etc. and have been thoroughly reviewed. These methods, in general, are associated with high capital, operational cost and drawbacks like the generation of secondary waste offering treatment problems [Bhaumik et al., 2013]. Unlike typical synthetic ion exchangers, plant based biomaterials have been of much interest and possesses advantages over the other methods being simple, cost effective and environment friendly method. **Bioremediation** is a method of environmental control and offers several advantages over conventional treatment methods including cost effectiveness, efficiency and minimization of chemical/biological sludge, no requirement of additional nutrients and regeneration of biosorbent [Afkhani, 2008]. Regeneration of the biosorbent increases the cost effectiveness of the process thus warrants its future success following the concept of *Green Chemistry* which is a new principle guiding the next generation products and processes [Pagnanelli, 2002]. Infact, actual wastewater treatment systems often have to deal with a mixture of heavy metals, however,

most research work still only focus on a single metal sorption. Since industrial effluents generally contain several metals, it is necessary to study the simultaneous adsorption of two or more metals from aqueous solutions [Srivastava, 2008]. In multi metal adsorption, the adsorption of one metal ion, generally, interferes with that of another.

We have already explored sorption of ternary metals onto unmodified FRLP but the efficiency and stability is less. In this paper, we reported decontamination of ternary metals from waste water with enhanced sorption efficiency and environmental stability using modified biomaterial.

**Keywords:** competitive biosorption, sorption capacity, *Ficus religiosa*, regeneration, ecofriendly

## EXPERIMENTAL

### Biosorbent preparation, sorption and desorption studies

Biosorbent preparation, sorption and desorption studies dealing has been carried out as mentioned in our earlier publications [Goyal et al., 2007, 2008, 2011; Goyal and Srivastava, 2008a, 2009; Kardam et al., 2009; Goyal and Masram, 2012].

### Synthetic modifications

#### *Acetylation*

Acetylation of amino group on the biomaterial was achieved by washing 12.0 gm of biomaterial first in 0.1 M HCl to remove any debris, followed by washing in sodium phosphate/sodium acetate buffer (0.1 M  $\text{Na}_3\text{PO}_4$ /1.0 M  $\text{NaC}_2\text{H}_3\text{O}_2$ ) at pH 7.2. The biomaterial is reacted with 64.0 ml of acetic anhydride and stirred while maintaining the pH of 7.2 for 1 hr. The acetylated biomaterial was next centrifuged for 5 min at 3000 rpm. After removing the supernatant, the biomaterial was then resuspended in 1 M hydroxylamine to remove O-acetyl groups. The biomaterial was then washed with 0.1 M HCl to remove any more soluble materials and finally washed with de-ionized water.

#### *Succination*

The succination of the amino groups on the biomaterial was achieved by washing 12.0 gm of biomaterial first in 0.1 M HCl to remove any debris, followed by washing in 0.1 M Sodium acetate at pH 8.0. The biomaterial was then resuspended in 500 ml of 1 M  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$  at pH 8.0. 16.0 gm of succinic anhydride was added to the suspended biomaterial. An additional 16 gm of succinic anhydride was added after 15 min intervals for the next

one and half hrs. (6 additions of 16.0 g succinic anhydride to the biomaterial). The biomaterial was then washed with 0.1 M HCl centrifuged and washed again with de-ionised water. Although the amino group is neutralized, it now forms an additional carboxyl group. By the addition of a carboxylate group, there should be an enhancement of metal binding by those metals that bind to carboxyl ligands.

#### *Graft Co-polymerization*

Graft Co-polymerization using standard practices were carried out as a function of *Ficus religiosa* leaves powder (FRLP) dosage (150, 200, 250, 300 mg), acrylic acid (1.0, 1.5, 2.0, and 2.5 ml), temperature ( $35\pm 0.5^{\circ}\text{C}$ ) and time (60, 90, 120 and 150 min.). A required amount of Ficus powder was dispersed in a definite amount of water. Appropriate amount of Ceric Ammonium Nitrate (200mg) and nitric acid (1.0 ml) were added slowly to the reaction mixture. Monomer Acrylic acid was added drop wise to the reaction mixture from the dropping funnel. The reaction flask was placed in a temperature controlled water bath at temperature ( $35\pm 0.5^{\circ}\text{C}$ ) for various time periods under stirring by a magnetic stirrer. The reaction mixture was filtered and the homo-polymer was removed with excess water. The grafted sample was dried to a constant weight and used for sorption studies. Percentage of grafting was calculated from the increase in initial weight of FRLP in the following manner:  $\%G = (W_2 - W_1) / W_1 \times 100$ , where  $W_1$  denotes the weight of native FRLP and  $W_2$  the weight of grafted FRLP after complete removal of the homo-polymer.

#### **Evidence in support of chemical modifications occurred onto biomaterial leading to enhanced sorption**

##### *Scanning Electron Microscopy (SEM)*

The comparison of the surface morphology of unmodified and modified FRLP was observed with a Scanning Electron Micrograph at bar length equivalent to 200  $\mu\text{m}$ , working voltage 20 KV with 200 x magnifications.

##### *Fourier Transform Infrared Spectroscopy (FTIR)*

FTIR analysis in solid phase in KBr was performed using a Fourier Transform Infrared Spectrometer (FTIR-8400, Shimadzu). Spectra of the sorbent before and after modifications were recorded.

#### **Evidence in support of improved environmental stability of the biomaterial**

##### *Thermo Gravimetric Analysis (TGA)*

The TGA was performed using Thermo Gravimetric Analyzer (DTG-60, Shimadzu). The comparison of Initial Decomposition Temperature (IDT) and Final Decomposition Temperature (FDT) of unmodified and graft co-polymerized biomaterial was estimated with thermo grams.

### **Biosorption Equilibria**

In the present trimetallic combination, sorption of metal is a competitive process between ions present in the solution. In such cases, one of the important physicochemical aspect for the evaluation of the sorption process as a unit operation is the equilibria of biosorption. Therefore, soluble metal fractions of ternary metal ions [Cd (II), Cr (III) and Ni (II)] after FRLP biosorption under different experimental conditions were measured to determine sorption capacity. Equilibrium isotherms of target ternary metals were obtained in the concentration range (1 to 100 mg<sup>l</sup><sup>-1</sup>) on the optimum biomaterial dosage (4.0 g) at pH 6.5 and plotted between metal adsorbed (mg) per unit mass (g) of sorbent against concentration. The concentration of metals in the sorbent phase was calculated as:  $q = (C_0 - C) V/W$ , where  $C_0$  and  $C$  denote the initial and equilibrium concentration of metals in the aqueous phase,  $V$  is the volume and  $W$  is the dry weight of the sorbent [Vieira and Volesky, 2003].

In order to define the efficiency of biosorption Lagergren plots were also obtained by conducting kinetic studies (batch) at initial [Cd (II), Cr (III) and Ni (II)] ions concentration. Modified FRLP (4.0 g) was suspended in 200 ml of [Cd (II), Ni (II) and Cr (III)] solution of known initial sorbate concentration at the appropriate pH values mentioned above, where maximum sorption was recorded. The mixture was continuously stirred using a magnetic stirrer. Samples were withdrawn at pre-determined time intervals in the range of 10 to 40 min, filtered and analyzed for residual metal ions concentration.

Sorption efficiency and number of regeneration cycles of the modified FRLP biomaterial was carried out in multi metal [Cd (II), Ni (II) and Cr (III)] using the procedure mentioned in our earlier publication [Goyal and Srivastava, 2008b].

### **RESULTS AND DISCUSSION**

The aerial part of the plant *Ficus religiosa* possesses various organic chemical moieties prominently large proportions of low molecular weight amino acids (Ejoba 2012). Amino acids have been found to constitute a physiologically active group of binding agents working even at low concentration, which because of ability to

interact with metal ions is likely to be active sites for the sorption of metal ions. Carboxylate anion [COO<sup>-</sup>] of the acid group has enough potential for binding cationic metal ions and become active sites for the sorption of M<sup>+</sup> ions. Enrichment of functional groups [COO<sup>-</sup>] responsible for sorption has been carried out as per following processes:

This is achieved through acetylation and succination of biomaterial.

In the acetylation of the biomaterial, the available amino ligands are blocked by acetic anhydride resulting into the increase in metal binding capacity. Acetylation brings about neutralization of the amino groups. It decreases the number of positively charged sites on biomaterial surface which causes a modest increase in metal uptake capacity (Figure 1).

Succination of the biomaterial is performed to add carboxyl group on to the nitrogen ligand (Figure 2).

Another synthetic strategy of graft co-polymerization was also applied to increase the number of negatively charged carboxylate groups on the FRLP biomaterial to enhance the ability to attract ternary metal [Cd (II), Cr (III) and Ni (II)] ions (Figure 3).

It was achieved by grafting of negatively charged functional groups using standard polymerization techniques. Grafting of acrylic acid onto FRLP biomaterial was calculated as a function of acrylic acid, time and biomass dosage at CAN (200mg), temp. (35±0.5<sup>o</sup>C) and nitric acid (1ml).

#### **Evidences in support of chemical modification occurred onto biomaterial**

*Scanning Electron Microscopy [SEM]:* FRLP represent large oval clusters in unmodified FRLP while condensed, irregular type morphology in succinated, acetylated and graft co-polymerized FRLP having pore area given in (Table 1). Observed aggregation and reduction in pore area of modified FRLP may be ascribed to the modification onto FRLP biomaterial.

*Fourier Transform Infra-Red Spectroscopy:* A perusal of the IR spectra of untreated and succinated biomaterial shows the presence of additional peak of carboxylate ion [1745.35 cm<sup>-1</sup>] and conversion of amino to amide group [3286.12 cm<sup>-1</sup> to 3355.27 cm<sup>-1</sup>] in succinated FRLP confirming succination of the biomaterial.

The conversion of amino to amide group [3286.12 cm<sup>-1</sup> to 3341.54 cm<sup>-1</sup>] confirmed acetylation process.

The appearance of characteristic peak at 1725.2 cm<sup>-1</sup> (C=O) in the IR spectra of graft co-polymerized compared to its unmodified FRLP confirms the formation of the grafted biomaterial.

#### **Sorption efficiency of modified biomaterial**



All the three modified biomaterials were subjected for the assessment of sorption efficiency of ternary metals under previously standardized optimum conditions. Increased sorption efficiency of ternary metals in all the three modified biomaterials has been observed (Table 2).

Increased sorption efficiency in the above three structural modifications can be assigned to the following facts:

Succination of the biomaterial results into the formation of additional carboxylate group along with the conversion of amine to amide group. Increase in carboxyl group results into the increase in sorption efficiency of biomaterial. Our finding is in agreement with the views of Gardea Torresday et al., 1998, who have reported that the succination not only decreases the number of positively charged sites in any biomaterial but also increases the number of negatively charged sites by contributing another carboxylic group.

In the case of acetylation the formation of amide group blocks the interferences of amino groups of the biomaterial. Our views find support from Tsezos, 1985, stating that acetylation reaction is an exchange of positively charge substituted ammonium ion which does not contribute to the biosorption of metallic ions by an amide function ( $\text{RNHCOCH}_3$ ) capable of coordination to the positively charged metal ion.

The enhanced sorption efficiency of graft co-polymerized biomaterial can also be explained on the basis of the fact that increase in the number of negatively charged ligands ( $\text{COO}^-$ ) increases sorption. Saito, 1985 has indicated that graft co-polymerization is a promising technique for modifying physical and chemical properties of the adsorbent and to improve the adsorption property as well as prevent the leaching of organic substances.

The above experiment provides important information that structurally modified FRLP is sufficient enough at the dose of 2g to show good sorption efficiency compared to the 4g dose of unmodified FRLP. The fact exhibits the cost effectiveness of the present biomaterial when structurally modified.

### **Evidence in support of improved environmental stability of the biomaterial**

#### *Thermo Gravimetric Analysis [TGA]*

Thermo Gravimetric analysis of untreated (native) and graft co-polymerized FRLP biomaterial showed significant difference in the Initial Decomposition Temperature [IDT] and Final Decomposition Temperature [FDT]. Upon grafting, temperature of FRLP biomaterial is raised from [IDT: 35.67 to 48.32<sup>0</sup>C; FDT: 602 to 611.35<sup>0</sup>C], indicating that grafting of Acrylic acid improves the thermal stability of FRLP biomaterial.

Increased stability of the graft co-polymerized biomaterial was also monitored on the basis of increase in number of regeneration cycle. A perusal of the Table 3 clearly shows that structurally modified biomaterial (polymerized) can be used 6 times compared to only 4 times of unmodified biomaterial, exhibiting its increase environmental stability (Figure 4).

It is inferred that out of 3 structural modifications considered for the study, graft co-polymerization not only increase the sorption efficiency but causes reduction in biomaterial dose highlighting its cost effectiveness.

In each case, data were evaluated at significance value ( $p < 0.05$ ). The maximum percentage sorption calculated for each ion present in ternary mixture onto modified FRLP was found to be higher (10-20%) as compared to unmodified FRLP reported in our earlier publication. Similar trends of effect of metal concentration, sorption time, biomaterial dosage, particle size and pH on biosorption efficiency were observed in modified FRLP as compared to unmodified FRLP. The order of sorption of toxic metals on the modified FRLP obtained in our case is as follows: [Cd (II) > Cr (III) > Ni (II)] which is again similar to unmodified FRLP. In case of multi metal solution, the binding site is competitively divided among the various metal ions. The combined action of competitive biosorption of [Cd (II), Cr (III) and Ni (II)] seems to be antagonistic in nature. The most logical reason for this action was claimed to be screening effect by the metals present in the solution [17].

### Equilibrium and Kinetic studies

One of the important aspects for the evaluation of sorption process as a unit operation is the equilibrium of sorption. The L type nature of the equilibrium isotherm curves obtained (Figure 5) in our experiments indicates favorable environment for ternary metal adsorption.

The adsorption capacity ( $q_e$ ) for the ternary system onto modified *Ficus religiosa* leaf powder remained higher than unmodified *Ficus religiosa* leaf powder and can be ascribed to the overlapping of adsorption sites of respective metal ions. Kinetics experiments showed that the adsorption of present ternary metals increases with the lapse of time. The adsorption of target cationic metallic species was rapid during 10 to 30 min of contact time after which the rate slowed down as the equilibrium approached 30 min of contact time. No further increase in sorption was observed with further increase of contact time up to 40 min. Adsorption rate constant ( $K_{ad}$ ) was determined from the following first order rate expression:  $\log (q_e - q_t) = \log (q_e) - (K_{ad}/2.303) t$ , where  $q_e$  and  $q_t$  ( $\text{mgg}^{-1}$ ) are the amount of target metals adsorbed per unit mass of grafted FRLP at equilibrium and at time  $t$  respectively.  $K_{ad}$  ( $\text{min}^{-1}$ ) was calculated from the slope of the linear plot of  $\log (q_e - q_t)$  versus time (Figure 6).

### CONCLUSIONS

The present study shows that modified FRLP provide an exciting opportunity for decontamination of ternary metals from aqueous system, particularly for rural and remote areas. Modifications resulted into the increased sorption efficacy [10 to 20%] and stability in terms of regeneration cycle [3 to 5] which in turn reducing the operational cost. FRLP efficiently removes ternary metal ions with the selectivity order of [Cd (II) > Cr (III) > Ni (II)]. The adsorption process followed a first order kinetics. The spent biosorbent was regenerated and effectively reused, making the adsorption process more economical. Thus, it seems to be a promising technique for modifying physico-chemical properties of the biosorbent.

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#### Figure Captions

**Figure 1:** Acetylation of biomaterial

**Figure 2:** Succination of biomaterial

**Figure 3:** Graft Co-polymerization onto biomaterial

**Figure 4:** Enhancement of reusability of the modified FRLP biomaterial for ternary metal ions

**Figure 5:** Equilibrium isotherms of ternary metal ions [Cd (II), Cr (III) and Ni (II)] on grafted FRLP [ $C_0$ : 25 mg/L; m: 4.0 g at pH 6.5

**Figure 6:** Lagergren plots for adsorption of multi metal at Grafted FRLP

**Table 1: Pore area ( $\mu\text{m}^2$ ) of unmodified and modified FRLP biomaterial**

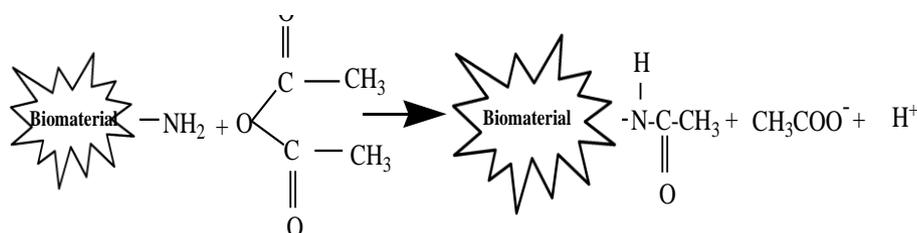
<b>Biomaterial</b>	<b>Pore area (<math>\mu\text{m}^2</math>)</b>
Unmodified FRLP	6.32
Succinated FRLP	2.45
Acetylated FRLP	2.59
Grafted FRLP	2.14

**Table 2: Enhancement of sorption efficiency of different chemically modified FRLP in case of multi metal solution at 4g biomass dosage**

TYPE OF BIOMATERIAL	Sorption efficiency (%) of ternary metal		
	Cd (II)	Cr (III)	Ni (II)
Unmodified FRLP	83.34	76.82	61.78
Succinated Biomaterial	91.12	86.65	78.82
Acetylated Biomaterial	88.64	83.51	71.63
Graft Biomaterial	95.23	91.23	79.23

Cycles	% Sorption		
	Cd (II)	Cr (III)	Ni (II)
1	95.23	91.23	79.23
2	95.12	91.13	79.08
3	95.02	91.01	78.94
4	94.89	90.96	78.76
5	94.65	90.76	78.26
6	93.23	89.65	77.84

**Table 3: Sorption of ternary metals on regenerated modified [Graft co-polymerized] biomaterial**



**Figure 1**

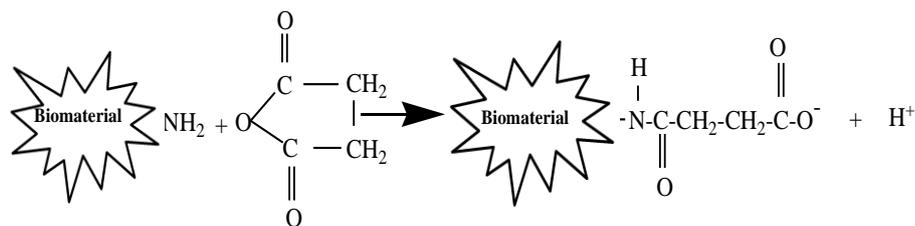


Figure 2

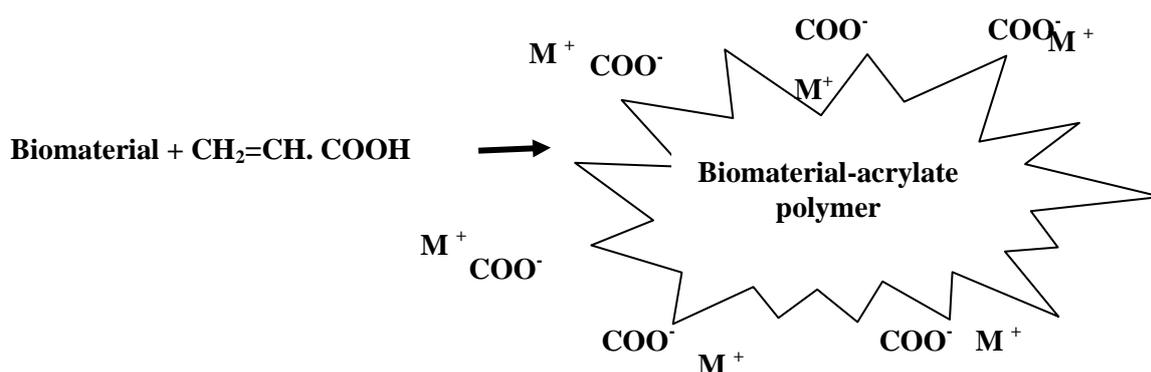


Figure 3

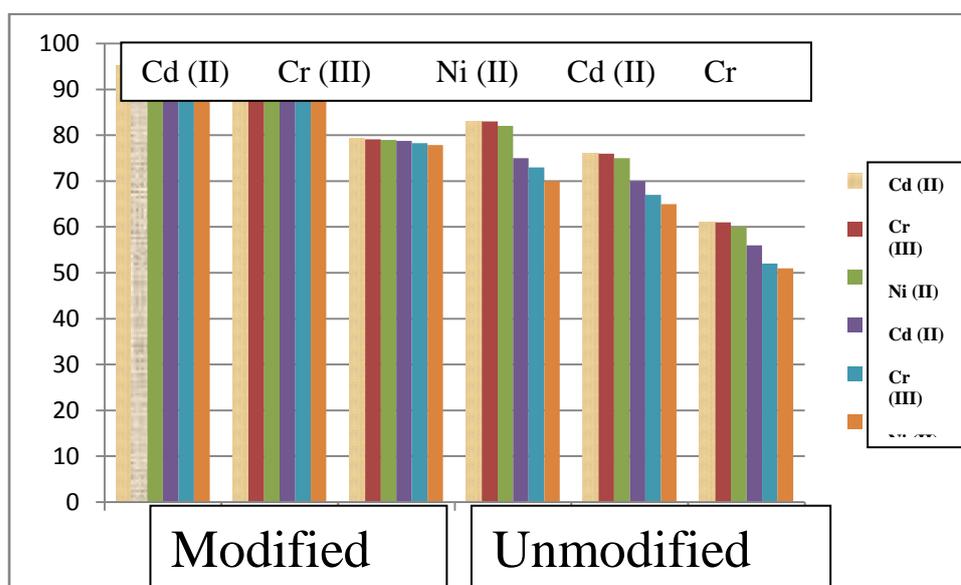


Figure 4

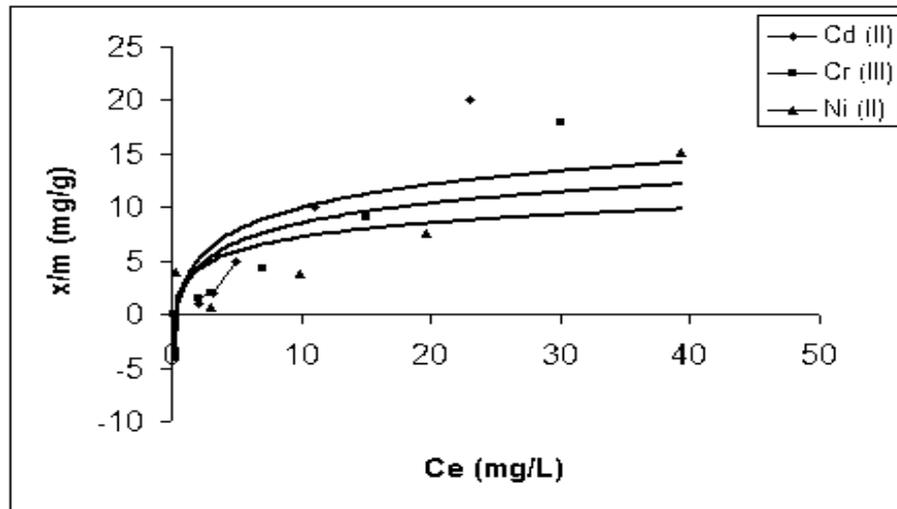


Figure 5

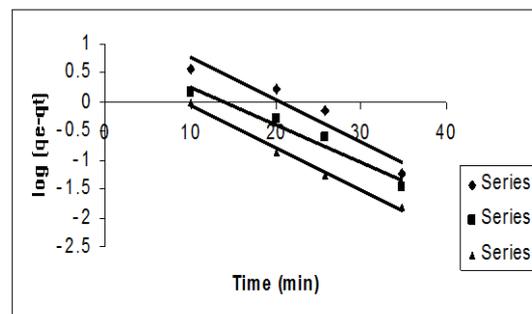


Figure 6