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Novel Adsorbents for Waste Water Treatment

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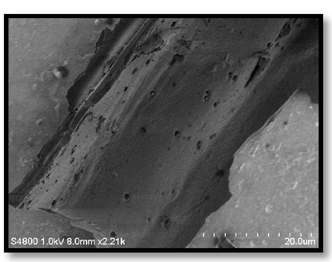
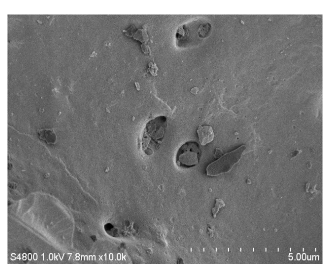
ABSTRACT

Large amount of waste water is generated by industrial, agricultural and domestic activities. Major content of waste waters is heavy metals and textile dyes which end up in natural bodies affecting living organisms. Hence, it is important to develop an effective method for removal of these pollutants from waste water. Various methods used for removal of metal ions and dyes include chemical precipitation, solvent extraction, ion exchange, oxidation/ reduction, membrane separation, adsorption etc. Among these methods, adsorption process is preferred due to its high efficiency, cost effectiveness and availability of various adsorbents. In our laboratory we have developed various cost effective novel adsorbents from sugar cane bagasse, hen feathers, and leaves of Couroupita guianensis, Cestrum nocturnum, saraca indica, Barleria cristata plants for removal of heavy metal ions (Cu, Ni, Cr) and textile dyes (methylene blue, indigo carmine, eosin Y, crystal violet, reactive red). For this purpose, batch adsorption process was used. Various parameters: pH, contact time, adsorbent dosage, particle size, adsorbent concentrations were optimized in order to achieve effective removal. In most of the cases removal was > 90 %. The adsorbents were characterized before and after adsorption using FTIR, FESEM, EDX, XRD techniques. The developed method was successfully applied to industrial effluents. The adsorbed metal ions/ dyes were recovered using various eluents such as HCl, HNO_3, KCl, NaOH. The study also covered kinetics and thermodynamics of adsorption process along with adsorption isotherms. Some of the results from our lab are summarized in this talk.

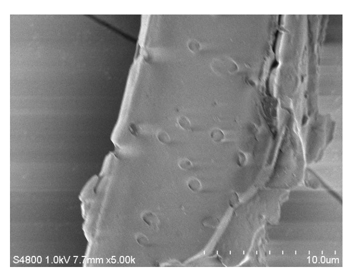
Graphical Abstract



Virgin ASB



Cr (III) loaded ASB



Cr (III) desorbed ASB

Keywords: Adsorbents, waste water treatment, adsorption isotherms, kinetics, thermodynamics

INTRODUCTION

Large amount of waste water is generated by industrial, agricultural and domestic activities. Major content of waste waters is heavy metals and textile dyes which end up in natural bodies affecting living organisms. Hence, it is important to develop an effective method for removal of these pollutants from waste water. Various methods used for removal of metal ions and dyes include chemical precipitation, solvent extraction, ion exchange, oxidation/ reduction, membrane separation, etc. but all these techniques have some or the other drawback [1] These methods are costly and accumulation of concentrated sludge becomes a disposal problem. Among all these methods, adsorption process is preferred due to its high efficiency, cost effectiveness, and availability of various adsorbents. Now a day bio adsorbents are used widely for removal of various ions [2] in our laboratory, we have used batch adsorption process for removal of number metal ions [3-7] and textile dyes [8-13]. The study deals with the adsorption isotherms, kinetics and thermodynamics for the selected adsorbate-adsorbent systems. Some of the reported results from our lab are summarized in this talk.

MATERIALS AND METHODS

Adsorbents and adsorbates: The various adsorbates used are Cu, Ni, Cr (metal ions) and methylene blue, indigo carmine, eosin Y, crystal violet, reactive red (textile dyes). The cost-effective novel adsorbents were developed from sugar cane bagasse, hen feathers and leaves of *Couroupita guianensis, Cestrum nocturnum, Saraca indica, Barleria cristata* plants. Commercial Activated Alumina (CAA) and chitosan were also used for this purpose.

Characterization of the adsorbent: All the adsorbents were characterized, before and after adsorption using FTIR (Shimadzu 8400) and FESEM (FET Nova nano SEM-450) coupled with EDX (Brouker SLASH-6130) techniques.

Adsorption studies: Batch adsorption method was used for the removal of various ions and dyes. The effective removal of metal ions/ dyes was achieved by optimizing various parameters viz; pH, contact time, adsorbent dosage, particle size and concentration. For each experiment, 25mL of adsorbate solution of known concentration was used. After addition of known amount of adsorbent, the solution was stirred continuously on a magnetic stirrer, and then centrifuged. Supernatant solution was analysed for concentration of the adsorbate using UV-Visible Spectrophotometer (Shimadzu). The percentage adsorption was determined using the following equation:

$$\%\,Adsorption = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

The adsorption capacity of the adsorbent was evaluated by using the following equation:

$$q_e = \frac{C_o - C_e}{m} \times V \qquad (2)$$

Where, q_e is the amount of adsorbate adsorbed by the adsorbent (g/g); C_o is the initial adsorbate concentration in contact with the adsorbate (g L^{-1}); C_e is the final adsorbate concentration in supernatant solution (g L^{-1}) after adsorption; m is the mass of the adsorbent (g) and V is the volume of adsorbate (L).

Recovery of adsorbate: Adsorbent loaded with adsorbate at optimized conditions was eluted with various volumes of HCl, HNO_3, KCl, NaOH. Concentration of the desorbed adsorbate was measured by UV- Visible spectrophotometer.

% desorption of adsorbate was calculated using the following equation:

$$\% \, Desorption = \left(\frac{Cd}{Ca}\right) * 100 \qquad (3)$$

Where, C_d is amount of adsorbate desorbed (g L^{-1}) and C_a is amount of adsorbate adsorbed (g L^{-1}).

RESULTS AND DISCUSSION

It has developed novel cost-effective adsorbents for the removal of above mentioned metal ions and textile dyes.

Modification of adsorbents: Sugarcane bagasse was washed with water, dried and powdered. However, no detectable adsorption was observed on it. Hence, it was modified for efficient adsorption. It was treated with orthophosphoric acid in 1:1 proportion (Acid Treated Sugarcane bagasse, ATSB). The obtained adsorbent was irradiated with gamma rays dose of 20 KGy using gamma chamber 900 (Irradiated Acid Treated Sugarcane Bagasse, IATSB). Radiation Induced Copolymerized sugarcane bagasse (RIGCSB) was prepared by grafting with 40% acytonitrile and DMF (1:3) giving a gamma radiation dose of 6 kGy [14].

Adsorbent using hen feathers was obtained [8] by washing them with distilled water and then drying. These were finely chopped and powdered for further use.

Selected plant leaves were washed with distilled water, dried, powdered and sieved through particular mesh size. Some of these adsorbents are further modified by treating them with orthophosphoric acid. These treated ones are further boiled with distilled water, dried and powdered. Some of the reported results from our lab are summarized below.

Removal various ions using different adsorbents: Optimization of various parameters for removal different ions using activated alumina are shown in figure1 [3].

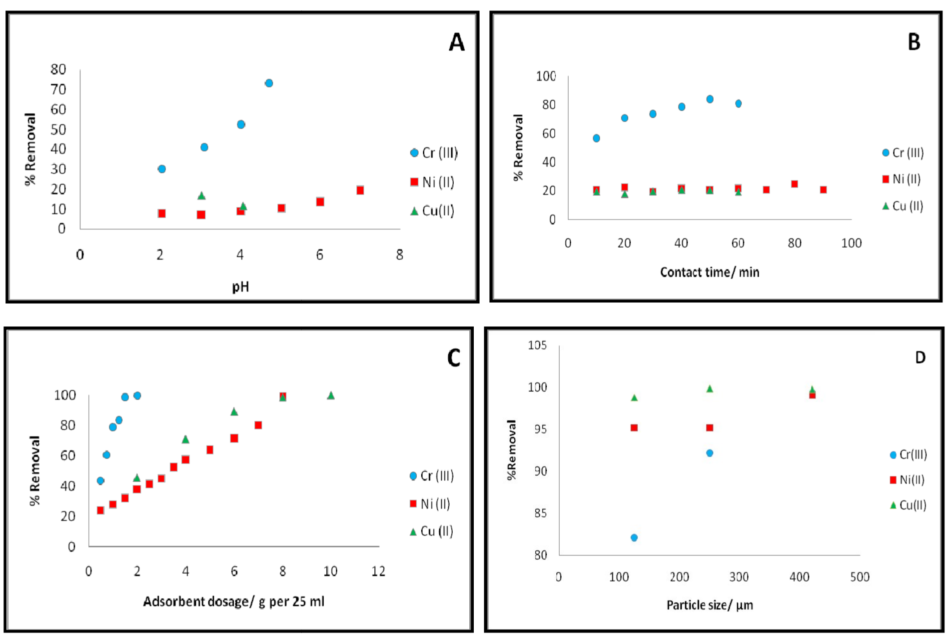
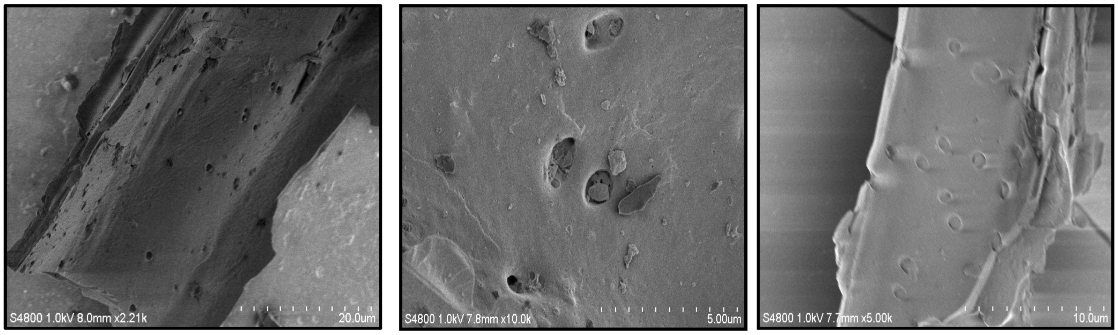


Figure 1. Optimization of various parameters for removal of different ions using Activated Alumina.

99.7 %, 99.5 % and 100.0 % removal of Cr (III), Ni (II) and Cu (II) was observed respectively under optimized conditions [Cr(0.01M): pH 4.7, contact time 50 min, adsorbent dose 2 g, particle size 250 µm, Cu(0.1M): pH 7, contact time 20 min, adsorbent dose 8 g, 420 µm, Ni(0.1M): pH 3, contact time 50 min, adsorbent dose 10 g, particle size 250 µm]. The characterization of various adsorbents was done by FTIR and SEM techniques. Some representative images are shown below [14].



Virgin ASB   Cr (III) loaded ASB   Cr (III) desorbed ASB

Figure 2. SEM images of virgin ASB Cr (III) loaded ASB and Cr (III)desorbed ASB.

These figures clearly indicate adsorption and desorption of ions on the adsorbent. A typical FTIR spectra after adsorption of different ions on ASB is shown below [14]

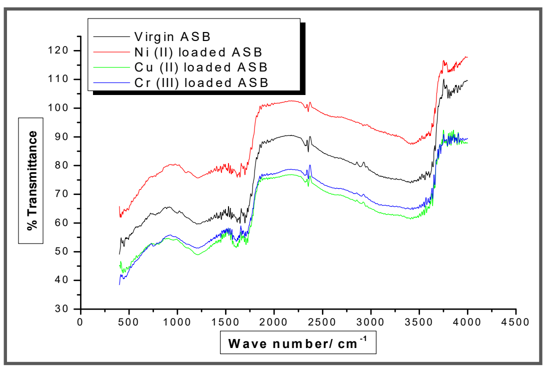


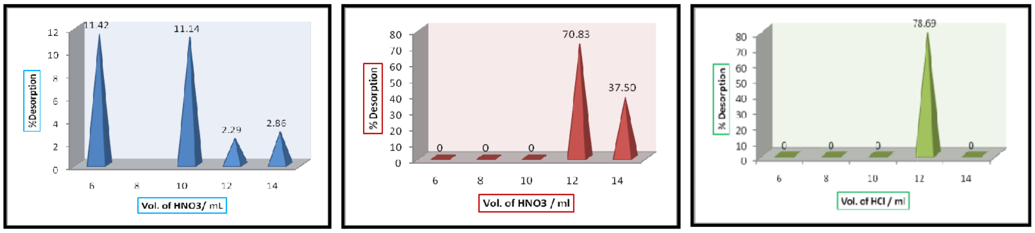
Figure 3. FTIR spectra of ion loaded ASB.

Change in the intensity of FTIR band for adsorption of different ions on various adsorbents indicated adsorption of ions on the adsorbent. The developed technique was applied to actual industrial samples and some typical reported results are shown in following table 1[14].

Table 1. Application of developed modified adsorbents for % removal of different ions from actual industrial samples.

Sample	Metal ion	CAA	ATSB	IATSB
1	Cr(III)	100	100	100
	Ni(II)	93.89	87.75	69.98
	Cu(II)	100	99.29	72.05
2	Cr(III)	100	100	100
	Ni(II)	94.59	94.65	97.52
	Cu(II)	32.92	41.02	78.14

The study also dealt with the recovery of metal ions and a representative example of desorption of ion loaded ASB is presented in figure 4 [14].



Cr III(HNO_3) Cu II(HNO_3) Ni II (HCl)

Figure 4. Desorption of ion loaded ASB using HNO_3/HCl.

In order to understand the mechanism of adsorption, various isotherm models were studied for different adsorbate-adsorbent systems.

Langmuir adsorption isotherm: The linear Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constants by the following equation

$$\frac{1}{q_e} = \frac{1}{ab}\frac{1}{C_e} + \frac{1}{b} \qquad \text{(linear form)} \qquad (4)$$

where q_e, the amount of adsorbate adsorbed per unit mass of adsorbent (g g^{-1}); *a*, a constant related to the affinity of the binding sites (L g^{-1}); *b*, the maximum amount of metal ion per unit mass of adsorbent (g g-1); C_e, the adsorbed metal ion concentration at equilibrium.

R_L Factor: The essential characteristics of Langmuir isotherm can be expressed in the form of dimensionless constant separation factor or equilibrium parameter (R_L) as given below.

$$R_L = \frac{1}{1+bC_0} \qquad (5)$$

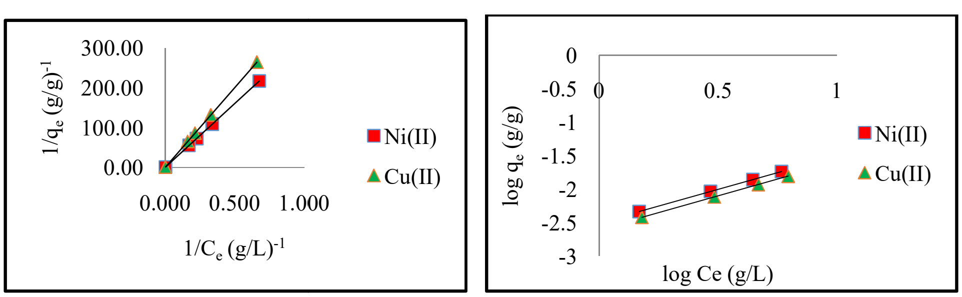
where C_0 is the initial concentration of the metal ions (g L^{-1}) and *b*, is the Langmuir constant (L g^{-1}). R_L values indicate the shape of the isotherm accordingly.

Freundlich isotherm: It is expressed by the following equation.

$$\log q_e = \frac{1}{n}\log C_e + \log K \qquad (6)$$

Where q_e, the amount of adsorbed per unit weight (g g^{-1}); *K*, Freundlich constants related to adsorption capacity; C_e, the equilibrium metal ion concentration (g L^{-1}); *n*, Freundlich constants related to adsorption intensity.

Typical Langmuir and Freundlich adsorption isotherm are shown below in figure 5 [3].



A B

Figure 5. Langmuir (A) and Freundlich(B) Isotherms for adsorption of Cu ((II) and Ni(II)on activated alumina.

Calculated R_L value from Langmuir adsorption isotherm indicated favorable adsorption. The values of a and b were found to be 4.36 x10^{-5} L g^{-1} and 71.43g g^{-1} for Ni (II) and 9.51x10^{-5} L g^{-1} and 26.32g g^{-1} for Cu (II) respectively. Freundlich constant and 1/n value were found to be 0.0031 and 0.999 for Ni (II) and 0.0025 and 0.999 for Cu (II) respectively.

Thermodynamics: Thermodynamic studies were done by varying the temperature of the system and using following equations

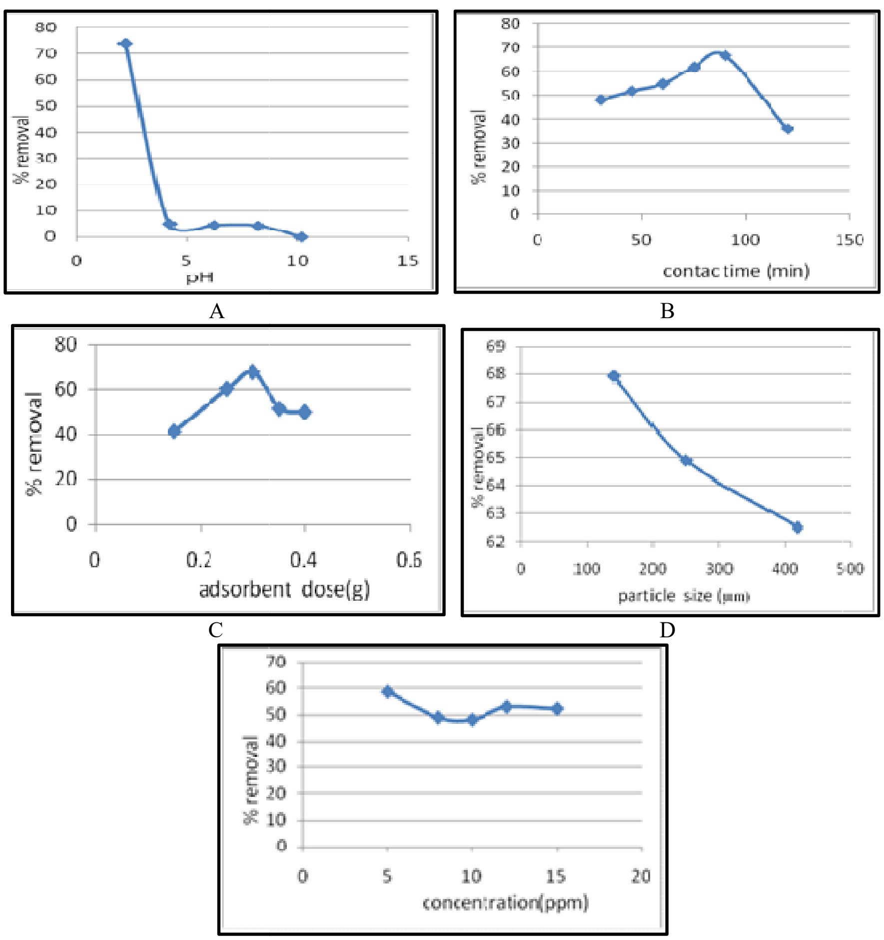
$$\ln K_c = -\frac{\Delta H^{o}}{RT} + \frac{\Delta S^{o}}{R} \qquad (7)$$

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} \qquad (8)$$

The obtained results for a specific system are described below
The ΔG^0 value was found to be -66.2 kJ mol^{-1} K^{-1} while ΔH^0 and $\mathbf{\Delta S^0}$ value was found to be -33.966 kJ mol^{-1} and 0.099 kJ $mol^{-1}K^{-1}$ respectively for adsorption of 0.1 M Cu (II) ions on ASB

Kinetics: Various kinetic models were verified, in most of the cases system followed pseudo second order model.

Removal of various dyes using different adsorbents: A typical example of optimization of various parameters for removal of Indigo Carmine dye using *Couroupita guianensis* leaves is presented below [10].



E

Figure 6. Removal of IC using *Couroupita guianensis* leaves: Effect of A. pH, B. contact time, C. adsorbent dosage, D. particle size and E. concentration on % removal.

The study revealed 60% removal of Indigo Carmine dye under optimized conditions. The adsorption process was found to be non-spontaneous and exothermic. It followed pseudo first order kinetics.
The results obtained for removal of different dyes using modified adsorbents prepared in our lab are shown below [9, 11-13].

Table 3. Results of some different dye-adsorbent systems

Dye	Adsorbent	% Removal	Adsorption isotherm	Kinetics	Thermodynamics
MB	Cestrum Noctamum	99.6	Freundlisch DR, Temkin	Pseudo second order	Spontaneous and exothermic
CV	Saraca Indica	97.6	Langmuir	Pseudo second order	Spontaneous and Exothermic
MB	Barlenia Crystata	91.8	Langmuir	Pseudo second order	Spontaneous and Exothermic
IC	Hen feathers	75.7	Langmuir	Pseudo second order	Non-Spontaneous and exothermic

APPLICATION

The developed adsorbents can be applied successfully to remove metal ions and dyes from waste water samples.

CONCLUSION

- Modified sugar cane bagasses, hen feathers and acid treated plant leaves were found to be potential adsorbents for removal of selected metal ions and dyes.
- Most of the studied adsorption systems followed pseudo second order kinetics.
- Most of the adsorption systems are spontaneous and exothermic.

ACKNOWLEDGEMENT

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REFERENCES

[1]. T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, *Bioresource Tech*., **2011**, 77, 247-255
[2]. N. Das, P. Artika, R.Vimala, V. Vinodhini, Use of natural products as biosorbent of heavy metals-An overview, *Nat. Product Radiance*, **2008**, 7, 133-138
[3]. N. S. Rajurkar, A. N. Gokarn, K. Dimya , Adsorption of Chromium(III), Nickel(II),and Copper(II) from Aqueous Solution by Activated Alumina, Clean: soil, air and water, **2011** 39,767-773
[4]. Nilima S. Rajurkar, Kumaree Dimya and Ashok Gokarn. "Radiation-induced graft coplymerization of monomer mixture onto sugarcane bagasse for removal of Cu(II) ions: A comparative study, *Asian Journal of Chemistry*, **2012,** 24(12), 5861-5864
[5]. N. S. Rajurkar, Kumaree Dimya, A.N. Gokarn Use of activated alumina for removal of nickel ions from aqueous solution: Kinetics and Desorption. *J. of Indian Council of Chemists*, **2011**, 28(2), 01-04.
[6]. N. S. Rajurkar, Dipali Mahajan, Removal and recovery of copper ions using chitosan as adsorbent, *J. Applicable Chem*., **2015** 4 (4), 1206-1217.

[7]. N. S. Rajurkar, Dipali Mahajan, Adsorption of Cobalt(II) and Nickel(II) ions from aqueous solution on chitosan, *J. of chemical, biological and physical science*, **2016** 6(4), 1203-1217.
[8]. N. S. Rajurkar, Madhavi Pawar, Removal of methylene blue dye from its aqueous solution using hen feathers, *Env. Observer,* 2013, 13, 215-216.
[9]. N. S. Rajurkar, Madhavi Pawar, Removal of indigo carmine dye from its aqueous solution using hen feathers as an adsorbent, *Env. Observer*, **2013** 14, 114-115
[10]. N. S. Rajurkar, N. S. Walvekar, Removal of methylene blue and indigo carmine from aqueous solutions using Couroupita guianensis leaves as an adsorbent, *J. Applicable Chem*., **2014**, 3 (6) 2602-2610,
[11]. N. S. Rajurkar, Asha Desai, Removal of crystal violet from aqueous solutions using chitosan and saraca indica leaves, *J. Applicable Chem.,* **2015**, 4(5), 1446-1455.
[12]. **D. J. Borkar , N. S. Rajurkar, P. V. Adhyapak**, A Novel Adsorbent: Barleria Cristata Leaves for Removal of Methylene Blue Dye, *J. Applicable Chem,* **2016**, 5 (5),1064-1074.
[13]. D. J. Borkar, N. S. Rajurkar, P.V. Adhyapak, Removal of methylene blue dye from aqueous solution by using Cestrum nocturnum leaves as a low cost adsorbent, *J. of chemical, biological and physical science,* **2017**, 7 (3), 512-525
[14]. Kumari Dimya, Removal and recovery of heavy metals from industrial waste water by using different techniques, Ph.D. thesis, University of Pune, **2013**.