International Journal of Environmental Sciences
ISSN: 2229-7359
Vol. 11 No. 1s, 2025
https://www.theaspd.com/ijes.php

Assessment Of Heavy Metal Removal From Aqueous Solutions Using Biomaterials

M.Padmaja[1], R. Pamila[2], S.Bala Padmaja[3], RM. Asha[4]
[1]. Assistant Professor, Department of Civil Engineering, Mahatma Gandhi Institute of Technology, Hyderabad, Telangana
[2.] Professor, Department of Civil Engineering, Sri Sairam Engineering College, Chennai, Tamilnadu
[3.] Assistant Professor, Department of Civil Engineering, Mahatma Gandhi Institute of Technology, Hyderabad, Telangana
[4.] Assistant Professor, Department of Civil Engineering, Sri Sairam Engineering College, Chennai, Tamilnadu

E-MAIL: mpadmaja_civil@mgit.ac.in[1], pamila.civil@sairam.edu.in[2], stbalapadmaja_civil@mgit.ac.in[3], asha..civil@sairam.edu.in[4]

Abstract
The paper evaluates two different food wastes for the removal of heavy metal ions from wastewater. This paper compares the current methods to explore the utilization techniques for various food wastes such as prawn and egg shells as bio adsorbents which are abundantly and easily available in India for the elimination of heavy metals from wastewater. In this study, the adsorption behaviour of two adsorbents such as Prawn and Egg shell with respect to Cu(II) and Zn(II) ions, has been studied in order to consider its application to the purification of metal finishing wastewater. The batch method was employed and the parameters such as pH, contact time, and initial metal concentration were studied. The influence of the pH of the metal ion solutions on the uptake levels of the metal ions by the different adsorbents used were carried out between pH 4 and pH 11. Adsorption parameters were determined using both Langmuir and Freundlich isotherms, but the experimental data were better fitted to the Freundlich equation than to Langmuir equation. The results showed that Prawn and Egg shells hold potential to remove cationic heavy metal species from industrial wastewater in the order Prawn shell < Egg shell.
Keywords*: Prawn shell, Egg shell, Adsorption, Langmuir, Freundlich*

1.0 INTRODUCTION

Copper(II) is one of the heavy metals most toxic to the living organisms and it is one of more widespread heavy metal contaminants of the environment. Extensive intake of Cu can cause hemolysis, hepatotoxic and nephro toxic effects, vomiting, cramps, convulsions, or even death (Ozar et al., 2007). The increase levels of copper in environment are posing a serious threat to mankind (Gustavo et al., 2007). It can cause harmful biochemical effects, toxicity and hazardous disease in human beings. Prescribed limit for copper in drinking water is 0.05mg/L as per WHO norms and also 0.05 mg/L as per ISI prescribed limits, 1993(Shrivastava, 2009).

Zinc is chemically active and alloys readily with other metals. The excessive intake of zinc may cause toxic effects such as carcinogenesis, mutagenesis and teratogenesis as a result of bioaccumulation (Nriagu, 1980). Zinc is widely used in many industries such as paint, batteries, fertilizers and pesticides, galvanization, pigment, polymer stabilizers, fossil fuel and combustion, electroplating, paper and pulp, pharmaceutical, textile mills, mining industries, etc. these industries are the main source of zinc pollution. The waste generated from these industries directly discharge to the environment and the water is polluted with zinc due to the excessive amount of zinc (Harte et al., 1991).

2.0 MATERIALS AND ETHODS

In this Section methods for using viable non-conventional low-cost adsorbents like Prawn shell and Egg shell for removal of metals such as Copper (II) and Zinc (II) are discussed.

2.1 Adsorbent Materials

Egg shell powder

The Eggshell used in the experiment collected from different hotels located in Chennai city, India. The samples were then washed with distilled water several times to remove dirt particles. The Eggshells were

then dried overnight in oven at 40° C. The dried Eggshells were ground into small particles and then finally sieved to fine powder of less than 0.425mm particle size and stored in air tight container for future use.

Prawn shell powder

The shell of Prawn was obtained from an aquaculture farm in Chennai (Tamil Nadu). It was air- dried and powdered in a grinder. The dry biomass was crushed into granules, sieved to different particle sizes, and then preserved in desiccators for use (i.e.PR- Raw). Air- dried and powdered prawn waste was soaked in concentrated H_2SO_4 for 12 hours and washed thoroughly with distilled water till it attained neutral pH and soaked in two percent $NaHCO_3$ overnight in order to remove any excess acid present. Then the material was washed with distilled water and dried at 110±20° C. The dry biomass was crushed into granules, sieved to different particle sizes, and then preserved in desiccators for use.(i,e.,PR- carbon).

2.2 Preparation of Adsorbate Solutions

Metal solutions

Stock solution of 10 mg/l Cu (II) ion is prepared dissolving copper sulphate pentahydrate ($CuSO_4.5H_2O$). To do this 39.28 mg $CuSO_4.5H_2O$ is added in distilled water contained in 1000 ml volumetric flask. Stock solution of 10 mg/l of Zn(II) is prepared by dissolving zinc sulphate heptahydrate ($ZnSO_4.7H_2O$). To do this 43.96 mg of Zinc sulphate heptahydrate solution is added to distilled water contained in 1000 ml volumetric flask. Hydrochloric acid and Sodium hydroxide were used to adjust the solution pH. Distilled water was used throughout the experimental studies.

2.3 Batch mode adsorption studies

Batch mode adsorption studies for individual metal compounds were carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dose, agitation time and pH. Solution containing adsorbate and adsorbent was taken in 250 mL capacity beakers and agitated at 150 rpm in a mechanical shaker at predetermined time intervals. The adsorbate was decanted and separated from the adsorbent using Whatman No.1 filter paper. To avoid the adsorption of adsorbate on the container walls, the containers were pretreated with the respective adsorbate for 24 hours.

2.4 Effect Of pH On Cu(II) And Zn(II) Adsorption

The effect of solution pH on adsorption of Cu(II) and Zn(II) was studied by mixing 2.5 g of individual adsorbent with 250 ml of mixed metal solutions having concentration of 3.6mg/L, 4.2 mg/L, of Copper and 3.3 mg/L and 3.7 mg/L of Zinc concentration at different pH value (5 – 8) at room temperature. The pH was adjusted with 1 N NaOH or 1 N HCl solutions and measured by pH meter. Agitation was made at a constant stirring speed of 170 rpm for 180 minutes. The remaining concentration of Cu(II) and Zn(II) after adsorption was measured using AAS. The percentage uptake of Cu(II) and Zn(II) was calculated according to the following equation:

$$\text{Percentage uptake (\%)} = \frac{C_o - C_t}{C_o} \times 100$$

Where, C_o is the initial concentration and C_t is the concentration at time t.

2.5 Effect Of Contact Time On Cu(II) And Zn(II) Adsorption

The effect of solution Contact Time on adsorption of Cu(II) and Zn(II) was studied by mixing 1.25 g of both adsorbents with 250 ml of mixed metal solution having concentration of 4.2 mg/L of Copper and 5mg/L of Zinc concentration at pH value of 6 at room temperature. Agitation was made at a constant stirring speed of 170 rpm. The remaining concentration of Cu(II) and Zn(II) after adsorption was measured at different time intervals of 30, 60 120 and 180 minutes using AAS. The percentage uptake of Cu(II) and Zn(II) was calculated according to the following equation:

$$\text{Percentage uptake (\%)} = \frac{C_o - C_t}{C_o} \times 100$$

Where C_o is the initial concentration and C_t is the concentration at time t.

2.6 Effect Of Adsorption Dose On Cu(II) And Zn(II) Adsorption : The effect of adsorption dose on Cu(II) and Zn(II) adsorption was investigated by different amount of adsorbents 1.5 gm and 2 gm in 250 ml of mixed metal solutions having initial concentration of 4.4 mg/l, 7.9 mg/l of Copper and 5 mg/l, 9.2 mg/l of Zinc. Agitation was made at a constant stirring speed of 170 rpm for 120 minutes. The

remaining concentration of Cu(II) and Zn(II) after adsorption was measured using atomic absorption spectrometer (AAS).

3.0 RESULTS AND DISCUSSION

3.1 Effect of pH on Cu(II) and Zn(II) Adsorption

The pH value of aqueous solution is an important parameter in adsorption process because it affects the surface charge of the adsorbent, the degree of ionization and specification of the adsorbate. The batch equilibrium studied for mixed metal solutions having concentration of 3.6mg/L, 4.2 mg/L, of Copper and 3.3 mg/L, 3.7 mg/L of Zinc concentration at different pH value ranging from 5 to 8 were carried at room temperature. Fig.1and Fig.2 shows that maximum percentage of Cu(II) and Zn(II) adsorption on Egg shell and Prawn shell were observed at pH 6.

Table I Effect of pH on the adsorption of Cu(II) and Zn(II) by Eggshells

S.No	Quantity of Egg shell powder(gm)	pH	Initial concentration of Cu(mg/L)	Initial concentration of Zn(mg/L)
			3.6	3.3
			Adsorption Efficiency(%)	
1	2.5	5	97	99
2	2.5	6	99.7	99
3	2.5	7	95.8	96.6
4	2.5	8	97	99

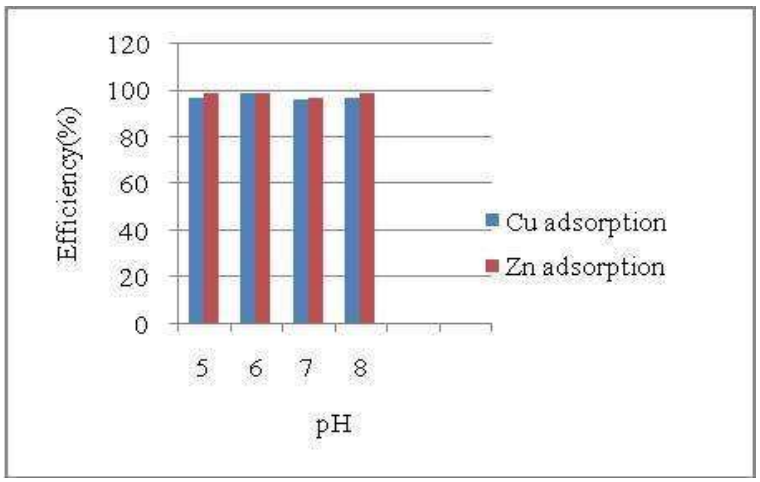


Figure 1. Effect of pH on the adsorption of Cu(II) and Zn(II) by Egg shells

Table II Effect of pH on the adsorption of Cu(II) and Zn(II) by Prawn shells

S.No	Quantity of Prawn shell powder(gm)	pH	Initial concentration of Cu(mg/L)	Initial concentration of Zn(mg/L)
			4.2	3.7
			Adsorption Efficiency(%)	
1	2.5	5	90	85
2	2.5	6	95.9	91
3	2.5	7	95.9	89
4	2.5	8	93	88

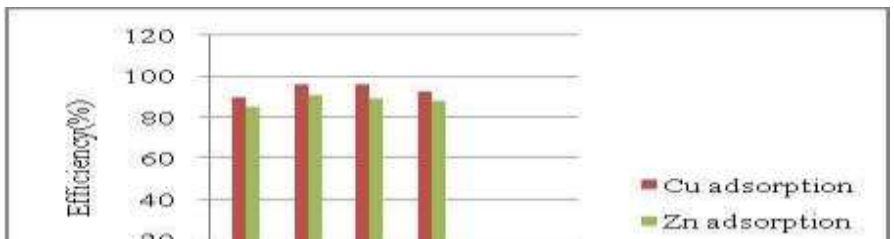


Figure 2. Effect of pH on the adsorption of Cu(II) and Zn(II) by Prawn shells

3.2. Effect of Contact Time on Cu(II) and Zn(II) Adsorption

Contact time plays an important role in adsorption process and the effect of contact time on adsorption capacity has been studied by varying the contact time from 30 to 180 minutes. The Copper and Zinc adsorption percentage at different contact time by Egg shells and Prawn shells is shown in Fig 3.
Results indicated that the Cu(II) adsorption by Egg shell and Prawn shells reached almost 95% and Zn(II) adsorption by Egg shells and Prawn shells reached almost 86% at 2 hours contact time.

Table III Effect of contact time on the adsorption of Cu(II) and Zn(II) by Egg shells and Prawn shells

S.No	Quantity of Egg shell powder(gm)	Quantity of Prawn shell powder(gm)	Contact Time (min)	Initial concentration of Cu(mg/L)	Initial concentration of Zn(mg/L)
				4.2	5
				Adsorption Efficiency(%)	
1	1.25	1.25	30	88.9	82
2	1.25	1.25	60	92.8	80
3	1.25	1.25	90	95.2	86
4	1.25	1.25	120	95.2	84

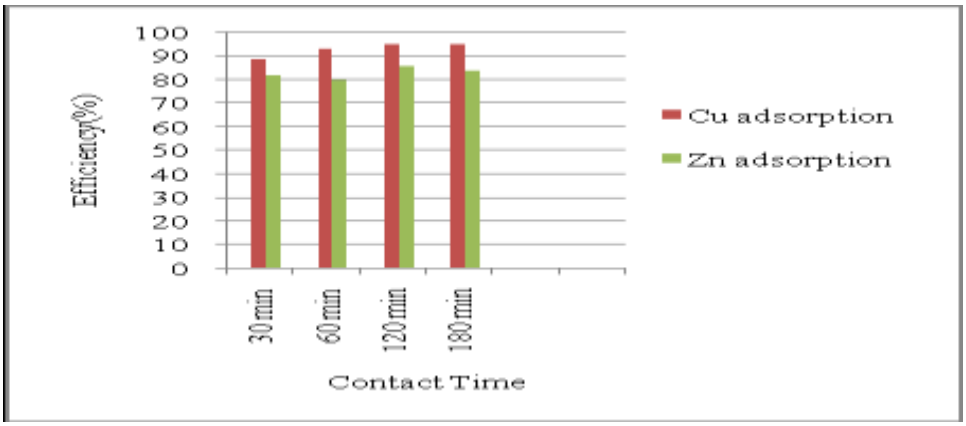


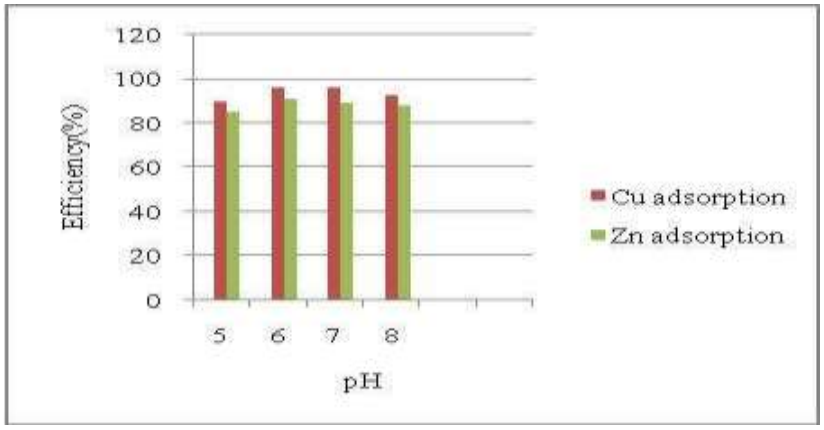
Figure 3. Effect of contact time on the adsorption of Cu(II) and Zn(II) by Egg shells and Prawn shells

3.3. Effect of Adsorption Dose on Cu(II) and Zn(II) Adsorption

The effect of adsorbent dosage was studied by varying the amount of adsorbent from 1.5 gm to 2.5 gm in 250 ml of mixed metal solutions of copper and zinc. After equilibrium the solutions were analyzed for the amount of Cu(II) and Zn(II). The results indicate that adsorption increased with increase in adsorption dosage.

Table IV Effect of adsorption dose on the adsorption of Cu(II) and Zn(II) by Egg shells and Prawn shells

International Journal of Environmental Sciences
ISSN: 2229-7359
Vol. 11 No. 1s, 2025
https://www.theaspd.com/ijes.php



S.No	Quantity of Egg shell powder(gm)	Quantity of Prawn shell powder(gm)	Initial concentration of Cu(mg/L)	Initial concentration of Zn(mg/L)
			4.4	5
			Adsorption Efficiency(%)	
1	1.5	1.5	95	88
2	2	2	97	90

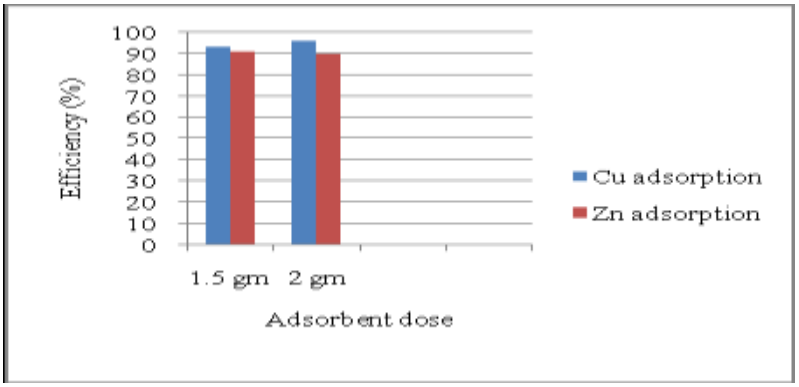
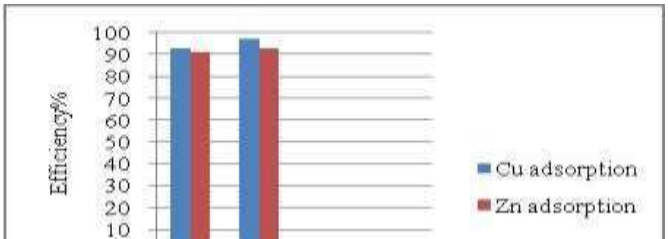


Figure 4. Effect of adsorption dose on the adsorption of Cu(II) and Zn(II) by Egg shells and Prawn shells

Table V Effect of adsorption dose on the adsorption of Cu(II) and Zn(II) by Egg shells and Prawn Shells

S.No	Quantity of Egg shell powder(gm)	Quantity of Prawn shell powder(gm)	Initial concentration of Cu(mg/L)	Initial concentration of Zn(mg/L)
			7.9	9.2
			Adsorption Efficiency(%)	
1	1.5	1.5	93	91
2	2	2	97	93



International Journal of Environmental Sciences
ISSN: 2229-7359
Vol. 11 No. 1s, 2025
https://www.theaspd.com/ijes.php

Figure 5. Effect of adsorption dose on the adsorption of Cu(II) and Zn(II) by Egg shells and Prawn shells

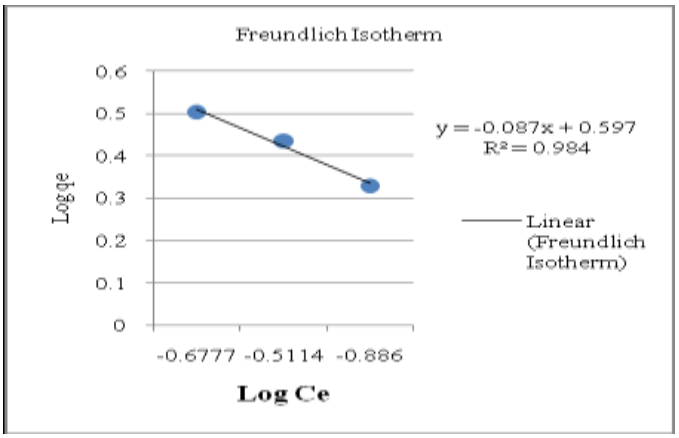


Figure 6. Freundlich Isotherm shown amount of Cu(II) adsorbed and equilibrium concentration

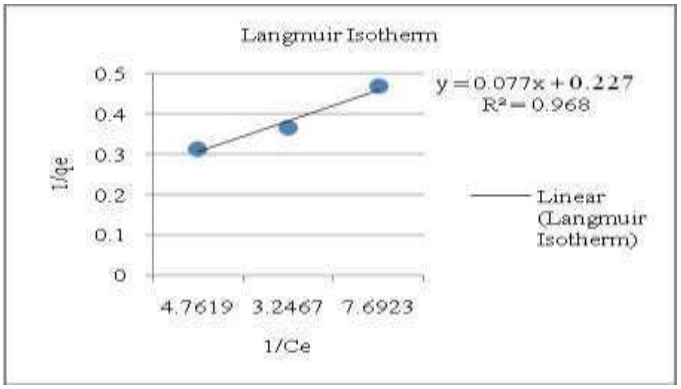


Figure 7. Langmuir Isotherm shown amount of Cu(II) adsorbed and equilibrium concentration

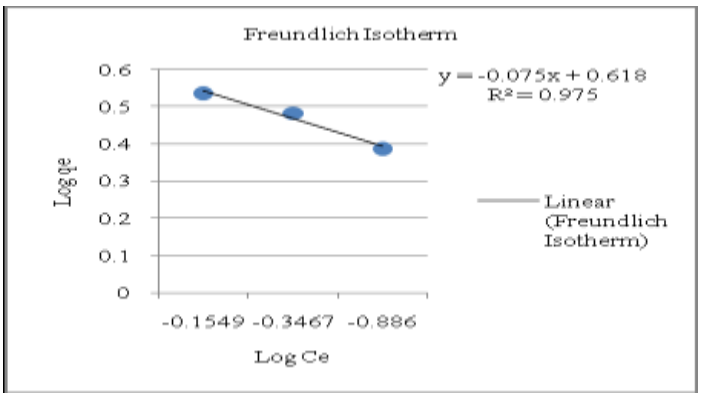


Figure 8. Freudlich Isotherm shown amount of Zn(II) adsorbed and equilibrium concentration

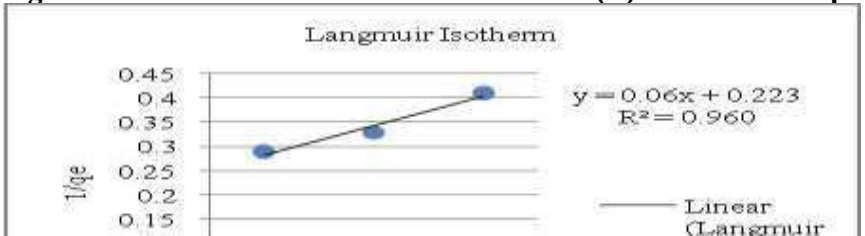


Figure 9. Langmuir Isotherm shown amount of Zn(II) adsorbed and equilibrium concentration

4.0 CONCLUSION

The removal of Cu(II) and Zn(II) from waste water by using Eggshells and Prawn shells has been experimented under several conditions such as at different pH, contact time and adsorption dose. The optimum pH for copper and zinc adsorption was found at pH 6. The optimum contact time was found to be 120 minutes at an agitation speed of 170 rpm. The adsorption data were fitted to different isotherm model equation and the Freundlich model was found to be the best model for both metals i.e. Cu(II) and Zn(II) with R^2 values 0.984, 0.975 respectively. Increase in adsorption dose increased the adsorption of metals. The results showed that Prawn and Egg shells hold potential to remove cationic heavy metal species from industrial wastewater in the order Prawn shell < Egg shell.

5.0 REFERENCES

[1] A. Chen, C. Yang, C. Chen, C. W. Chen. The chemically crosslinked metal-complexed chitosan for comparative adsorptions of Cu(II), Zn(II), Ni(II) and Pb(II) ions in aqueous medium. Journal of Hazardous Materials, 163 (2009), 1068-1075.
[2] A. Rajendra and C. Manisya, "Extraction of Chromium from Tannery Effluents Using Waste Egg shell Material as an Adsorbent", British Journal Of Environment and Climate Change, pp.44-52, 2011.
[3] AnimeshAgarwal and Puneet Kumar Gupta, "Removal of Cu and Fe from Aqueous solution by using eggshell powder as low cost adsorbent", pp.75-79, 2014.
[4] D. Lucaci, M.Visa and A. Duta. Copper removal on wood–fly ash substrates – thermodynamic study. Rev. Roum. Chim., 56 (2011), 1067-1074.
[5] F. Fenglian, Q. Wang. Removal of heavy metal ions from wastewater, Journal of Environmental Management, 92 (2011), 407-418.
[6] J. Carvalho, A. Riberio, J. Grace, J. Araujo, C. Vilarinho and F. Castro, "Adsorption Process onto an Innovative Eggshell-Derived Low- Cost Adsorbent in simulated effluent and real industrial effluents", 2011.
[7] NorhafizahbintiAbd. Hadi, NurulAimibintiRohaizar and Wong CheeSien, "Removal of Cu(II) from Water by Adsorption on Papaya Seed", Asian Transaction on Engineering, Vol:1, Issue 05, pp.49-55, 2011.
[8] Hema Krishna R, A.V.V.S Swamy, "Investigating on the adsorption of hexavalent chromium from the aqueous solutions using powder of papaya seeds as a sorbent", International Journal of Environmental Science and Research, Vol: 2, No. 1, pp.119-125, 2012.
[9] Siew-TengOng, Shiau-Ping Yip, Pei-Sin Keng, Siew-Ling Lee, Yung-Tse Hung, "Papaya seed as a low -cost sorbent for Zinc Removal", African Journal of Agricultural Research, pp.810-819, 2012.
[10] J. N. Egila, B. E. N. Dauda, Y.A. Iyaka and T. Jimoh "Agricultural waste as a low cost adsorbent for heavy metal removal from wastewater", International Journal of the Physical Sciences", Vol. 6(8), pp.2152-2157, 2011.
[11] Randhir Kumar, Dharmendra Singh, Richa Gupta, ArchanaTiwari, "Egg Shell and Spent Tea: An Eco-friendly cost effective adsorbent", International Journal of Biological and Pharmaceutical Research, pp.896-901, 2013.
[12] NurulAimibintiRohaizar, NorhafizahbintiAbd. Hadi, Wong CheeSien,"Removal of Cu(II) from Water by Adsorption on Chicken Eggshell", International Journal of Engineering and Technology, Vol:13, No:01, pp.40-45, 2013.
[13] SitiNurAeisyahAbas, MohdHalim Shah Ismail, MdLias Kamal and ShamsulIzhar, "Adsorption Process of Heavy Metals by Low-Cost Adsorbents: A Review", World Applied Sciences Journal 28(11), ISSN 1818-4952, pp.1518-1530, 2013.
[14] I. Nhapi, N. Banadda, R. Murenzi, C.B. Sekomo and U.G. Wali. Removal of Heavy Metals from Industrial Wastewater Using Rice Husks The Open Environmental Engineering Journal, 4 (2011), 170-180.
[15] S. V. Yadla, V. Sridevi, M.V.V. Chandana lakshmi. A review on adsorption of heavy metals from aqueous solution. Journal of chemical, biological and physical science, 2 (2012), 1585-1593.