

Iron Removal from Water by using Cashew Nut Shell

Aleena R. Haneef¹, Sukanya S. Nair²

^{1,2}UKF College of Engineering and Technology, Paripally, Kollam, Kerala, India

Abstract: Cashew nut shell from the agricultural waste was used as the adsorbent for the removal of iron present in the water. The effect of various parameters such as particle size, adsorbent dosage, initial iron concentration, contact time, pH and temperature were studied. FTIR, Scanning electron microscopy and Energy-dispersive X-ray spectroscopy were used for the characteristic study of cashew nut shell. Pinnacle 900 H atomic absorption spectrophotometer was used for the analysis. Results of adsorption isotherm study shows that, Langmuir isotherm was best fitted to the experimental data. Pseudo second order equation was follows adsorption kinetics. Desorption study was conducted by varying the hydrochloric acid concentration. Based on the study's results showed that cashew nut shell was effectively used for the iron present in water.

Keywords: Cashew nut shell, Iron, Adsorption, Adsorption kinetics, Desorption study

1. Introduction

For human health, agriculture, industries and sustainability of the earth's ecosystem water is very essential. Now in many regions of the world, this precious commodity is running scarce. And yet the availability of water is too often taken for granted. Water consumption has almost doubled in the last fifty years. But quality of water continues to worsen. Even where there is enough water to meet current needs groundwater resources are increasingly polluted. In ground water iron was one of the common contaminants, the world health organization limit the value of iron in drinking water is 0.3 mg/L [1]. Economic and technological problems are caused due to the high concentrations of iron in water. They precipitate a dark sludge on contact with air, thus the corrosion of the pipes are caused due to the development of ferruginous bacteria on walls of pipes. Iron is one of the essential mineral for human, but its presence in ground water above a certain limit makes the water un-usable for aesthetic considerations such as odour, metallic taste, plumping fixtures and staining of laundry [2].

There are several techniques used for the removal of metals from water. It include: precipitation, ion exchange method, filtration, electrochemical operation, biological operations, evaporation, membrane processes etc. These methods have lack of significance due to their high capital and operational cost, continuous need of chemicals, disposal of residual metal sludge[3]. Adsorption was one of the cost-effective and environmentally friendly methods used for water treatment. In the present study, cashew nut shell from the agricultural waste was used as the adsorbent for the removal of iron present in the water. The effect of various parameters such as particle size, adsorbent dosage, initial iron concentration, contact time, pH and temperature has been studied. Adsorption isotherms and kinetic study were carried out to evaluate experimental data and adsorption mechanism[4].

2. Experimental

2.1 Adsorbent

Cashew nut shell was used as the adsorbent in this study. It was collected from nearby cashew factory and then it was rinsed with water to remove dust present in it. It was then allowed to dried at room temperature. After that it was burned for producing ash, and it was powdered by using a grinder. Fig 1, 2, 3 were shows the cashew nut shell, cashew nut shell ash, cashew nut shell powder.



Figure 1: Cashew nut shell



Figure 2: Cashew nut shell ash



Figure 3: Cashew nut shell powder

2.2 Adsorbate

APHA method was used for the preparation of for synthetic iron sample. Stock solution of 200 mg/L was produced by using ferrous ammonium sulphate. For this 20 ml of concentrated sulphuric acid added to the 50 ml of water. In this solution, 1.404 gram ferrous ammonium sulphate was

added. 0.1 molarity potassium permanganate was added drop wise in this solution, until a faint pink colour was persist. From this, standard iron solution of 10ppm was prepared by diluting 50 ml of stock solution to 1000ml. From this standard, standards of desired concentration was prepared[5].

2.3 Analysis

Concentration of iron present in the solution after adsorption was determined by using Pinnacle 900 H atomic absorption spectrometer (PerkinElmer). Solution pH was measured by using pH meter. Different functional groups present in the cashew nut shell were identified by using FTIR. Surface morphology of cashew nut shell adsorbent was determined by scanning electron microscope. Energy-dispersive X-ray spectroscopy was used for the elemental analysis.

2.4 Adsorption study

In this present study, batch adsorption experiments were carried out by varying the adsorbent dosage, initial iron concentration, adsorbent particle size, pH, contact time and temperature. All batch adsorption experiments were conducted in 500 ml Erlenmeyer flask containing 50 ml adsorbate solutions at room temperature to evaluate iron removal efficiency. For each trial, a sample was periodically taken out of the flask and filtered, 0.5 mL of concentrated nitric acid and 0.5 mL of concentrated sulphuric acid was added to it. Then this solution was allowed for digestion. During digestion volume of solution was lowered to 20 to 25 mL. Then it was allowed for cooling. After cooling solution was again made up to 50 mL. 12.5 mL of calcium chloride solution was added to it. Calcium chloride solution was prepared by diluting 630 mg of calcium carbonate in 50 mL of 20 % volume of hydrochloric acid solution (In this 10 mL hydrochloric acid mixed with 40 mL distilled water). After the addition of calcium chloride, solution was taken for analysis [5]. By using the mass balance equation percentage removal of iron can be find out using the equation

$$\text{Percentage removal} = [(C_0 - C_e) / C_0] * 100$$

Where C_0 was the initial concentration of iron in mg/L and C_e was the equilibrium concentration in mg/L in the aqueous solution.

2.4.1 Effect of particle size

For studying the effect of particle size, particles retained in the 90, 150, 300 and 600 microns are selected. 50 mL adsorbate solution of 2 ppm was prepared. 0.1 gram adsorbent was added to it. Then sample was allowed for agitation in a shaker revolving at 60 rpm in 60 minutes. After the agitation, solution was allowed for filtration. After filtration and digestion cooling was carried out and solution was taken for analysis.

2.4.2 Effect of adsorbent dosage

For studying the effect of adsorbent dosage, particles retained in the 90 micron sieve was selected. 50 mL adsorbate solutions of 2 ppm was prepared. Adsorbent dosage varied from 0.1 to 0.5 gram added in each conical flask. Then sample was allowed for agitation in a shaker revolving at 60

rpm in 60 minutes. The samples were then agitated and filtered and the filtrate were analysed as mentioned before.

2.4.3 Effect of initial iron concentration

For studying the effect of initial iron concentration, particles retained in the 90 micron sieve was selected. 50 mL adsorbate solutions of different initial iron concentrations were prepared. Initial iron concentrations were varied from 1 to 5 ppm. Adsorbent dosage of 0.2 gram was added to it. Then sample was allowed for agitation in a shaker revolving at 60 rpm in 60 minutes. The samples were then agitated and filtered and the filtrate were analysed as mentioned before.

2.4.4 Effect of contact time

For studying the effect of contact time, particles retained in the 90 micron sieve was selected. 50 mL adsorbate solutions of initial iron concentration of 2 ppm were prepared. Adsorbent dosage of 0.2 gram was added to it. Then sample was allowed for agitation. During agitation, contact time was varied from 10 to 90 minutes. After the agitation, solution was allowed for filtration. After filtration digestion and cooling was carried out and solution was taken for analysis.

2.4.5 Effect of pH

For studying the effect of pH, particles retained in the 90 micron sieve was selected. 50 mL adsorbate solutions of initial iron concentration of 2 ppm were prepared. pH of the solution was varied from 1 to 9. For getting acidic pH 0.1 molarity hydrochloric acid was used. For getting basic pH, 0.1 molarity sodium hydroxide was used. Adsorbent dosage of 0.2 gram was added to it. The samples were then agitated and filtered and the filtrate were analysed as mentioned before.

2.4.6 Effect of temperature

For studying the effect of temperature, particles retained in the 90 micron sieve was selected. 50 mL adsorbate solutions of initial iron concentration of 2 ppm were prepared. Adsorbent dosage of 0.2 gram was added to it. Then sample was allowed for agitation. During agitation temperature was varied. Temperature varied from 30 to 70⁰ C. After the agitation, solution was allowed for filtration. After filtration, digestion and cooling were carried out and solution was taken for analysis.

2.5 Adsorption isotherms

Freundlich and Langmuir adsorption isotherm models were carried out to determine the model that was suitable for design process. The linear equation used in Langmuir adsorption isotherm was

$$C_e / Q_e = C_e / Q_m + 1 / (Q_m K_L)$$

Where Q_e was the amount of adsorbate adsorbed per unit weight of the adsorbent (mg/kg) and intensively depends on the physical and chemical properties of the adsorbent. Q_m was the maximum adsorption capacity for the solid phase loading and K_L is the energy constant related to heat of adsorption. In Langmuir isotherm, separation factor (R_L) was a dimensionless constant that gives information about nature of adsorption.

$$R_L = \frac{1}{1 + K_L C_0}$$

Where K_L was the Langmuir constant and C_0 is the initial concentration of metal ion. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$) [6].

The linearized form of the Freundlich was represented by the following equation:

$$\ln Q_e = \ln K_f - (1/n) \ln C_e$$

n value indicates the degree of non-linearity between solution concentration and adsorption as follows: if $n = 1$, then adsorption is linear; if $n < 1$, then adsorption is a chemical process; if $n > 1$, then adsorption is a physical process [7].

2.6 Adsorption kinetics

For conducting kinetic study, 50 mL adsorbate solutions of initial iron concentration of 2 ppm were prepared and adsorbent particle size of 90 microns was selected. Adsorbent dosage of 0.2 gram was added to it. The flasks were placed in the orbital rotating shaker for 60 minutes. Temperature was seted as 30°C. Samples were collected at different time periods and analysis was carried out.

Physical and chemical characteristics of the adsorbent as well as the mass transfer process depends the mechanism of adsorption. Pseudo first order and second order equations are used to study the kinetics of adsorption. In pseudo first order equation, diffusion control process was the mechanism of adsorption.

The equation used for pseudo first order was,

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Where q_e was the amount of adsorbate adsorbed at equilibrium (mg/g), k_1 (min^{-1}) was the rate constant of first order adsorption, q_t was the adsorption capacity at time t (mg/g).

In pseudo second order equation, sorption process was chemisorption.

The equation used for pseudo second order was given below:

$$t/q_t = (1/k_2 q_e^2) + (1/q_e) t$$

Where $k_2 q_e^2$ (mg/g min) was the initial adsorption capacity rate and k_2 was the pseudo second order rate constant (min^{-1}). [8].

2.7 Desorption studies

Desorption study was conducted for recycling the spent cashew nut shell and the metal ions. Spent cashew nut shell was transferred to the conical flasks that contain 50 mL hydrochloric acid of different molarity. Concentration of hydrochloric acid varied from 0.1 to 0.8 molarity.

Results and discussion

3.1 Characteristics study of cashew nut shell

FTIR spectrum of cashew nut shell was shown in figure 4. The intense broad band at 3486.85 was due to the presence of alcoholic groups. Band at 1685 indicates the presence of carbon carbon ring was in the surface. COO stretching vibration is present at 1452 cm^{-1} . Band at 3700 cm^{-1} indicates the presence of inorganic component silica present in it [9].

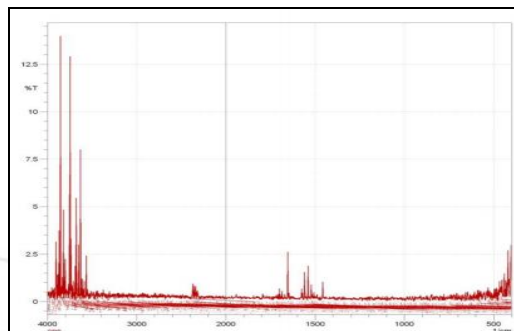


Figure 4: FTIR of cashew nut shell

3.2 Scanning Electron Microscopy (SEM)

SEM image of the cashew nut shell was shown in fig 5. From the figure, it was seen that surface of cashew nut shell was appears irregular and porous. So it was confirmed that surface of the cashew nut shell has sufficient surface area for metal adsorption.

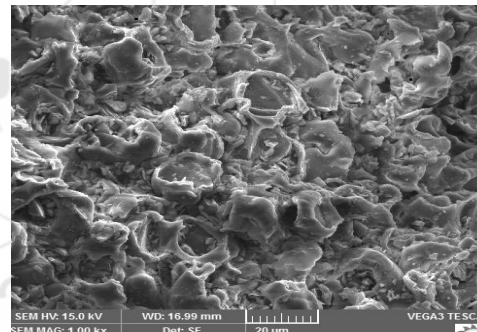


Figure 5: SEM image of cashew nut shell

3.3 Energy-dispersive X-ray spectroscopy (EDS)

EDS image of the cashew nut shell was shown in fig 6. Various elements present in cashew nut shell was Carbon, Oxygen, Calcium, Potassium, Zirconium, Magnesium, Sodium, Aluminium, Silica and Niobium.

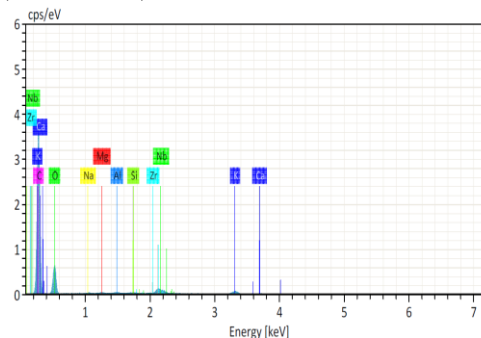


Figure 6: EDS image of cashew nut shell

3.4 Effect of particle size

It was observed that by increasing the particle size adsorption efficiency goes to decreases. Maximum efficiency was found to be 93.95% in 90 microns. It was due to the fact that when particles are in finer form more will be the surface area available for adsorption.

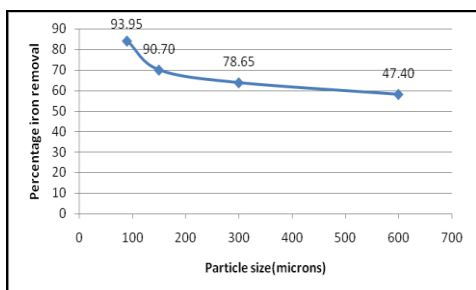


Figure 7: Particle size vs. percentage iron removal graph

3.5 Effect of adsorbent dosage

Effect of cashew nut shell was an important factor for absorption. It was observed that adsorption efficiency decreases with increase in adsorbent dosage. Maximum efficiency was found to be 92.8 % in 0.2 gram. Increasing the adsorbent dosage, initially efficiency goes to increases up to 0.2 gram; it was due to the availability of increased number of sites and exchangeable sites for the adsorption of iron. Further increase in adsorbent dosage did not cause significant improvement in adsorption. It seems to be due to the binding of almost all irons to the cashew nut shell and equilibrium was reached after increasing the adsorbent dosage above 0.2 gram.

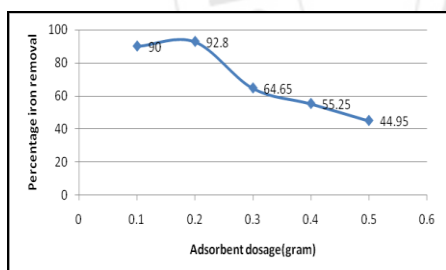


Figure 7: Adsorbent dosage Vs percentage iron removal graph

3.6 Effect of initial iron concentration

Maximum efficiency was found to be 87.95 % in 1 ppm. After that increasing the initial iron concentration, efficiency goes on decreasing. Decrease in the percentage of iron removal was due to the saturation of available active sites on the cashew nut shell after 1 ppm of initial iron concentration.

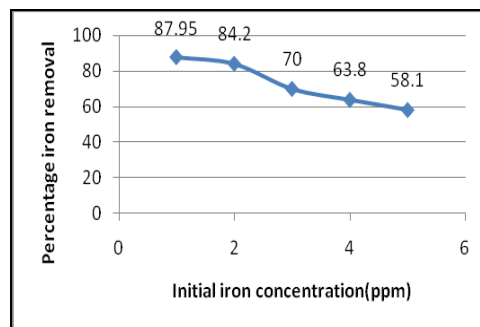


Figure 8: Initial iron concentration Vs percentage iron removal graph

3.7 Effect of contact time

The effect of contact time was on efficiency of iron adsorption was investigated to study the rate of iron removal. It was observed that initially by increasing the contact time, efficiency goes on increasing. Maximum efficiency was found out to be 82.7%. Equilibrium was reached after 50 minutes. In the beginning adsorption efficiency was higher, due to the availability of large surface area of cashew nut shell, after increasing contact time above 50 minutes equilibrium was reached.

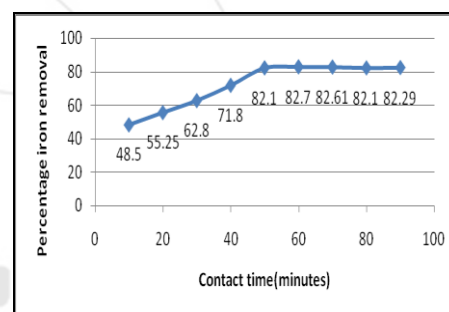


Figure 9: Contact time Vs. percentage iron removal graph

3.8 Effect of pH

pH of the solution affects the solubility of metal ions in the adsorption. It was observed that by increasing the pH adsorption efficiency increases initially, after pH of 5 efficiency goes on decreasing. Study beyond pH of 9 was not conducted due to the precipitation of irons forming hydroxides.

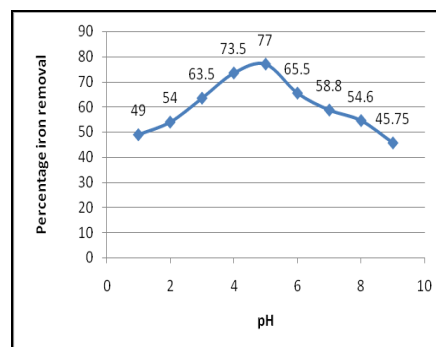


Figure 10: pH Vs. percentage iron removal graph

3.9 Effect of temperature

It was observed that by increasing the temperature, adsorption efficiency increases initially up to 40°C, then after efficiency goes to decrease. Maximum efficiency was achieved at 40°C. This was due to the decrease in surface activity suggesting adsorption was exothermic in nature in this adsorption. Graph of temperature Vs percentage removal efficiency was shown in fig 11.

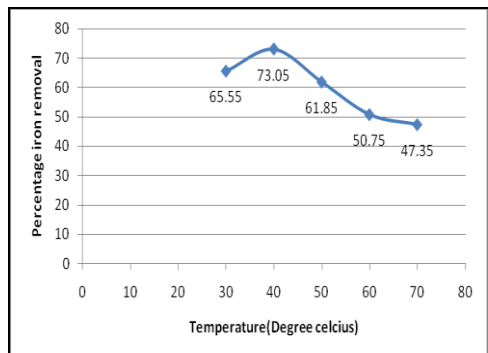


Figure 11: Temp. Vs. percentage iron removal graph

3.9 Adsorption isotherms

Fig 12 and 13 shows the Langmuir and Freundlich isotherms. By using Langmuir adsorption isotherm, maximum adsorption capacity was found to be 200 mg of iron/g for cashew nut shell. R^2 value was found to be 0.987 and K_L was found to be 5. R_L was found to be 0.0909, it indicates adsorption was favourable.

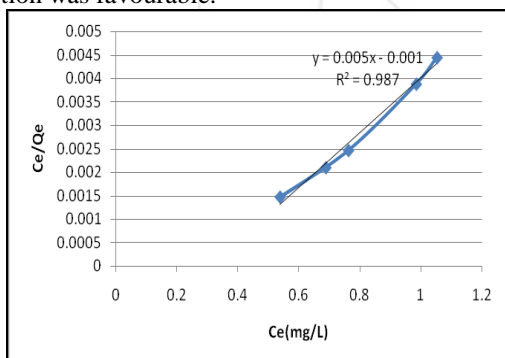


Figure 12: Langmuir isotherm curve in iron analysis

By using Freundlich isotherm, value of n was 1.529, value of k_f was 1.9232 and R^2 value was 0.976. n value was greater than 1, which indicates physical adsorption.

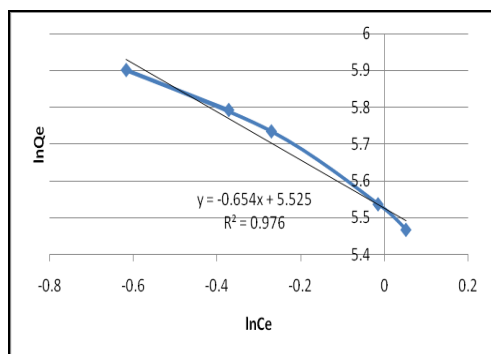


Figure 13: Freundlich isotherm curve in iron analysis

Comparing both isotherms, Langmuir isotherm has high R^2 value, Therefore Langmuir isotherm was best fitted to the experimental data.

3.10 Adsorption kinetics

Fig 14 and 15 shows the pseudo first and second order curve.

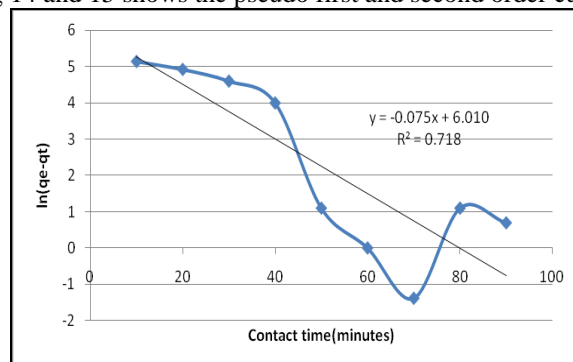


Figure 14: Pseudo first order curve

By using pseudo first order equation, the values of q_e were found to be 1.077 mg/gram and k_1 was found to be 6.010.

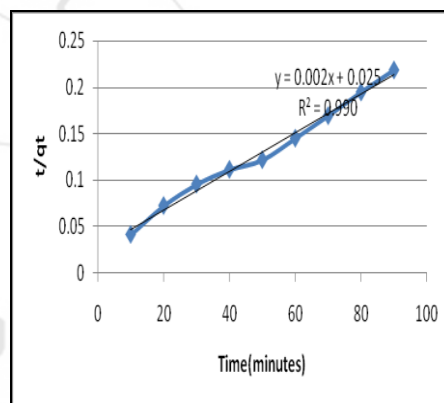


Figure 15: Pseudo second order curve

By using pseudo second order equation, the values of q_e were found to be 500 mg/gram and k_2 was found to be .00016. It was clear from the figures 14 and 15 that pseudo second order model was valid with high R^2 value compared to pseudo first order model. Therefore it was concluded that rate limiting step for the adsorption of iron into cashew nut shell follows chemisorptions.

3.11 Desorption study

Table 1 shows the desorption value of Iron from spent cashew nut shell using hydrochloric acid. Results shows that by increasing the concentration of hydrochloric acid, desorption rate increases initially, but it decreases at 0.5 molarity.

Table 1: Desorption of Iron from spent cashew nut shell using hydrochloric acid

Initial iron concentration (mg/l)	Percentage Recovery Of Iron							
	0.1M	0.2M	0.3M	0.4M	0.5M	0.6 M	0.7M	0.8M
2	18.9	21.5	35.4	42.8	47.0	42.8	35.07	32.82

4. Conclusion

The present study showed that cashew nut shell as an agricultural waste can be used for removal of iron from the aqueous solutions. The removal of iron strongly depends on the particle size, adsorbent dosage, initial concentration of adsorbate, pH, contact time and temperature. Maximum removal efficiency was achieved at particle of 90 microns and adsorption efficiency decreases with increase in the initial ion concentration. 0.2 gram was the optimum dosage, and 60 minutes was the optimum contact time. In iron adsorption, maximum efficiency was achieved in a pH of 5, by increasing the temperature efficiency goes to decreases.

Equilibrium adsorption efficiency was found to be 73.05% Maximum monolayer adsorption capacity was found to be 200 mg of iron/g for cashew nut shell. Langmuir isotherm has high R^2 value; therefore it was best fitted to the experimental data. Pseudo second order was the best fitted to the experimental data, it shows chemisorptions. Desorption study indicated that by increasing the hydrochloric acid concentration, desorption rate decreases. Based on the results obtained from these studies, it was concluded that cashew nut shell can be effectively used as an adsorbent for the treatment of water containing iron .

References

- [1] MohammadrezabRahimizadeh, AbdolmajidLiaghat, "Biosorbents for adsorption of heavy metals: A review", International conference of environmental science engineering and technologies, 5-6 may. University of Tehran, Tehran, Iran (2015)
- [2] NamalPriyantha., Linda B.L. Muhammad KhairudDahri And D.T.B. Tennakoon "Dragon fruit skin as a potential low cost biosorbent removal of manganese(ii) ions", Journal of applied science in environmental sanitation, Volume 8, Number 3, pages: 179-188. (2013)
- [3] R. Balaji, S. Sasikala, G. Muthuraman, "Removal of Iron from drinking / ground water by using agricultural Waste as Natural adsorbents", International Journal of Engineering and Innovative Technology (IJEIT) Volume 3, Issue 12 (2014)
- [4] PonnusamySenthil Kumar, SubramaniamRamalingam, Vasanthakumar Sathyaselvabala, Selvaraj Dinesh Kirupha, Korean J, "Removal of cadmium(II) from aqueous solution by agricultural waste cashew nut shell", *Chem. Eng.*, 29(6), 756-768, (2012).
- [5] American public health association (APHA), standard method for the examination of water and waste water
- [6] I. Langmuir, "The adsorption of gases on plane surfaces of glass, mica and platinum", *Journal of the American Chemical Society*, vol 40, pages: 1361-1403, (1918)
- [7] H.M.F. Freundlich, "Over the adsorption in solution", *Journal of Physical Chemistry*, vol 57, pages: 385-470, (1906)
- [8] P. SenthilKumar, S. Ramalingam, R. V. Abhinaya, S. Dinesh Kirupha, T. Vidhyadevi and S. Sivanesan "Adsorption Equilibrium, Thermodynamics, Kinetics, Mechanism and Process Design of Zinc(II) ions onto Cashew Nut Shell", *The Canadian journal of Chemical Engineering*, Vol 90, pages: 973-983, (2012).

- [9] Ena Smidt, Katharina Böhm and Manfred Schwanninger and Ena Smidt, *The Application of FT-IR Spectroscopy in Waste Management*, University of Natural Resources and Life Sciences, Vienna, (2011).