Removal of Nickel (II) from Aqueous Solution by adsorption onto Nano adsorbent prepared from Cucumis Melo peel

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Abstract : In the present study, attempt has been made to use Cucumis Melo peel for the preparation of activated carbon with a view to use it in the removal of Nickel (II) ion from aqueous solution. The air-dried chopped Cucumis Melo peels are carbonized by pyrolysis method using muffle furnace, prepared nano adsorbent using ball milling and characterized by the methods suggested by the Bureau of Indian Standard. The effect of initial pH, initial concentration of Nickel (II) ion solution and contact time for the adsorption of Nickel (II) ion onto CMAC are studied in a batch process mode. Result shows that pH 6 is the most suitable, while the maximum adsorbent capacity is at a dosage of 250 mg/L. The equilibrium data for the adsorption of Nickel (II) ion from aqueous solution onto CMAC are fitted to Langmuir, Freundlich and Temkin isotherm models and the model parameters are evaluated. The results showed that the equilibrium adsorption of CMAC is best described by Langmuir and Freundlich isotherm model.
Key words : Nickel (II) ion, Cucumis Melo, Nano Adsorbent, Activated Carbon.

1. Introduction

One of the important toxic metals, Nickel (II) finds its way to the water bodies through effluents from industries. It is present in the effluents of silver refineries, zinc base casting and storage battery industries. As it resists corrosion even at high temperature, it can also be used in gas turbines, rocked engines and desalination plants. It is also used in coinage and costume jewelers. Skin contact with Nickel causes a painful disease called "Nickel itch" which leads to death[1]. The Nickel salts are known to be acutely and chronically toxic to human. Acute poisoning of Ni (II) causes headache, dizziness, nausea, and tightness of the chest, chest pain, shortness of breath, dry cough, cyanosis, and extreme weakness[2]. At higher concentration, it is a potent carcinogen and causes cancer of lungs, nose and bone. Nickel Carbonyl $[Ni(CO)_4]$ has been estimated as lethal in human at atmospheric exposure of 30 ppm for 30 min[3]. The toxic nature of fish, crops and algae were also reported[4]. Prenatal toxicity associated with Nickel chloride exposure on female rats was also reported[5]. In recent years, much attention has been focused on the removal of heavy metals using industrial wastes, agricultural wastes etc. Many authors used natural adsorbents like activated carbon prepared from activated clay[6], agricultural solid waste[7], peanut hull[8] and Flyash[9]. The biosorption of Nickel was maximum at a biosorbent concentration of 4g/L and at pH of 5.0 reported[10] the above results in conclusion of their study on the removal of Ni (II) from aqueous solution using the powdered leaves of *Azadirachta indica*. The modern technology developed by the man, not only depleted the wealth of nature but also created environmental degradation. The problem of water pollution due to heavy metals and their impact on environment is presently

the focus of international attention. In choosing a waste water treatment technology, factors like nature of pollutants, permissible limits and economy of the treatment method have to be considered.

Recent research of selective and sensitive methods for the determination of metals in water at trace levels is studied. Among available methods, adsorption appears to have least adverse effects. The use of waste material from industries and agriculture for the removal of metal ion which reduces the treatment cost, and also provides a solution for the solid waste management of the industries. Most of the industries cannot afford to use conventional wastewater treatment methods owing to their high cost. In an effort to evolve an useful **u**ser-friendly, **e**co-friendly and **e**conomical process, the present study was taken up. The present study includes the adsorption studies on Nickel (II) using Cucumis Melo peel Activated Carbon. The adsorption of Nickel ion onto this activated carbon was studied in batch mode condition. Langmuir, Freundlich and Temkin isotherms were used to analyze the equilibrium data. The present work helps the individual organization to remove the excess concentration of the Ni (II) from their effluents within their premises without much effort and time.

2. Materials and Methods

2.1 Preparation of Nano adsorbent

Cucumis Melo Peel was collected from in and around pazhamudir nilayam of Coimbatore. The collected peels were cut into small pieces, washed with tap water several times to remove dust and dirt rinsed with deionised distilled water and then dried. The dried peels were placed in the muffle furnace and carbonization was carried out at $200^{o}C$ for 2 hrs. The carbonized material was ground to a fine powder. The resulting material was further processed using high energy ball mill (Vibration micro-Pulveriser ''Pulverisette 0'' Fritsch) is composed of an agate mortar containing an agate ball (5 cm in diameter) where about 6.5 g of carbon powder was introduced. It was placed in an air tight container for further use.

2.2 Preparation of synthetic waste water

Analytical reagent grade of Nickel solution, $NiSO_4.6H_2O$ (1000 mg L^{-1}) was used as synthetic waste water. The synthetic waste water was first prepared by diluting the stock solution of Ni^{2+} with distilled water to desired concentration. The pH of the waste water was then adjusted to 6 by addition of drops of 0.1 M NaOH or 0.1 M HCl solution.

2.3 Characterisation of the adsorbent (CMAC)

The adsorbent was characterized using FTIR spectroscopy and Scanning Electron Microscopy (SEM).The IR spectrum of **CMAC** was recorded using FT-IR (FTIR - 8400 S Shimadzu, Japan) within the range 3700 cm^{-1} and 420 cm^{-1}, with KBr disc as reference. The surface morphology of the adsorbent was observed on Scanning electron microscope (SEM-JEOL JSM6360 LA, Japan) and BET (Brunauer-Emmett-Teller) Surface analyzer was used to determine the specific surface area of the carbon surface.

2.4 Batch Kinetic studies

The effect of various parameters on the removal of Nickel (II) onto the CMAC was studied: Batch adsorption experiments were conducted at room temperature. For each experiment, 100ml of initial concentration of metal solution at pH 6.0 were taken in 250ml Erlenmeyer flask. 250mg of CMAC adsorbent is added and was shaken at a constant agitation speed (200 rpm). The supernatant was analyzed and the effect of adsorbent dose on the removal of metal was measured with different amounts, different pH and various concentration by contacting time(10 - 210 minutes) till attained equilibrium. The optimum condition for maximum removal of Nickel (II) from an aqueous solution of 100mg/L were determined as follows: room temperature (30ºC), adsorbent dose (250mg), contact time (210 min), adsorbent size (75μm), pH 6.0 and agitation speed (200rpm).

3. Results and Discussion

3.1 Adsorbent Characterization

3.1.1 Morphological studies

Studies on an adsorbent's surface topography could provide important information on the degree of interaction between the adsorbent particles and the Nickel molecules[11]. Scanning Electron Microscope (SEM) was used to study the surface morphology of CMAC. The textural structure of the adsorbent is presented as scanning electron micrograph at x 3000 magnification and x 2500 magnification (Figure.1 a & 1 b). The SEM image showed the irregular texture and porous nature of the surface of the adsorbent (Figure.1 a &1b).The seemingly rough surface of the adsorbent is an indication of high surface area[12].
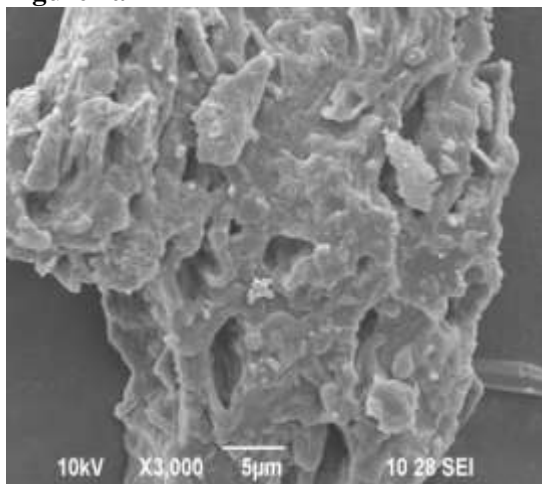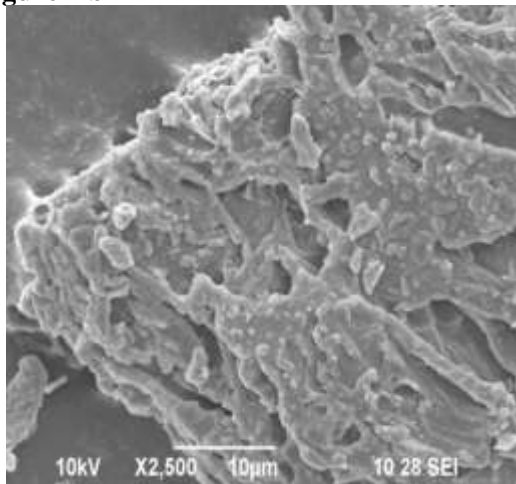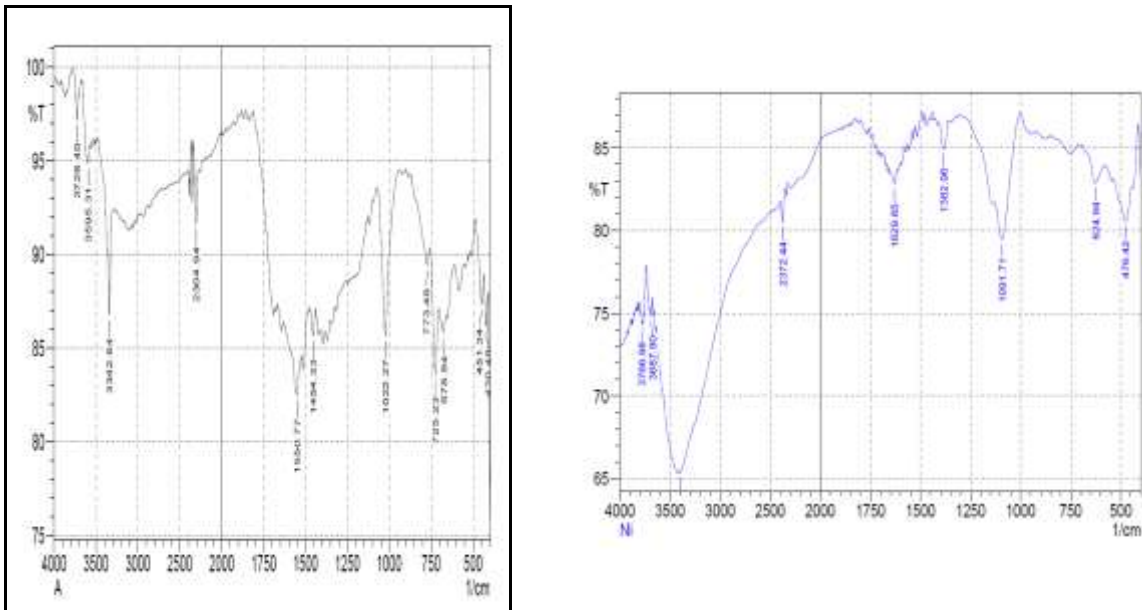
Figure 1a   **Figure 1 b**

SEM images of Nickel (II) loaded CMAC 4.3(e) at 5 µm (a), 10 µm (b)

3.1.2 Infrared Spectroscopic Studies

The FTIR spectrum of CMAC before the adsorption process (Figure. 2a) displays a number of absorption peaks, indicating the complex nature of the material under study. The FTIR spectroscopic analysis indicated a sharp and strong band stretch in the region between $3700 cm^{-1}$ and $3595 cm^{-1}$ representing the presence of free –OH groups. The sharp peak at 3342 cm-1 is due to N-H stretching. The position of absorption depends upon the degree of hydrogen bonding. The band at 2304 cm^{-1} corresponds to the presence of -C=C stretching vibration arising from groups such as alkynes,cyanides and isocyanates. The band obtained at 1550.77 cm^{-1} was due to the asymmetric stretching of NO_2 group. The band observed at 1022.27 cm^{-1} was due to C-O stretching of C=C-O-C group. The band observed at 770-730 cm^{-1} shows monosubstitution on the aromatic ring. The IR spectrum of the adsorbent CMAC supported the presence of –OH, –C=C, $–NH_2$,– NO_2 and -C-O-C functional groups present on the surface of CMAC respectively that are potential adsorption sites for Nickel ion.

2 (a) before Nickel adsorption   **2 (b) after Nickel adsorption**
Figure.2: FTIR spectrum of Cucumis Melo peel Activated Carbon (CMAC)

Figure.2b is the FTIR spectrum of CMAC after the adsorption of Nickel. When compared with the FTIR spectrum of the adsorbent before any adsorption (Figure. 2a), there were slight shifts in the position of –OH, –C=C, –NH$_2$, – NO$_2$ and -C-O-C functional groups in CMAC before and after adsorption. These may be as a result of the attachment of Nickel ion to the adsorbents through these functional groups.

3.2 Effect of different experimental condition

Since adsorption is affected by physical and chemical variables, the influence of pH, initial Ni (II) concentration and adsorbent dose are investigated in this study.

3.2.1 Effect of pH

The solution pH is an important controlling parameter in the adsorption process. The pH value affects the surface charge of the adsorbent, the degree of ionization, and metal speciation in aqueous solution during the adsorption process. The pHzpc is an important characteristic of any adsorbent because it indicates the surface charge of the adsorbent in the solution. The pHzpc of CMAC was 5.0. The effect of pH on the removal of Ni(II) is investigated by testing different values of pH at room temperature and 100 mg/L concentration of Ni(II) aqueous solution. Ni (II) exists as Ni^{2+} and NiOH$^+$ at pH 6, beyond which Ni(OH)$_2$ tends to dominate. Therefore, a set of similar batch equilibrium studies, using a solution with pH values in the range of 2.0 – 6.0 were conducted to study the influence of the pH on the adsorption capacity and behavior of CMAC for Ni(II) ion. Figure.3 depicts the effect of pH on the adsorption of Ni (II) by CMAC. The adsorption of metal ion increases with an increase in the solution pH. The metal ion become less stable as there is an increase in the solution pH and adsorption reaches equilibrium at 6.0. However, at still higher pH values there is a decrease in the removal of metal ion which is due to their precipitation of metal ion as their hydroxides. The influence of the pH on adsorption could be explained by the presence of the functional groups involved in the metal ion uptake. The maximum percentage removal of metal ion using CMAC was found to 96.2% for Ni (II) at optimum pH. The results obtained in the present study related to the effect of the solution pH on the adsorption of metal ion by a low-cost adsorbent, are in agreement with those of earlier studies[13].
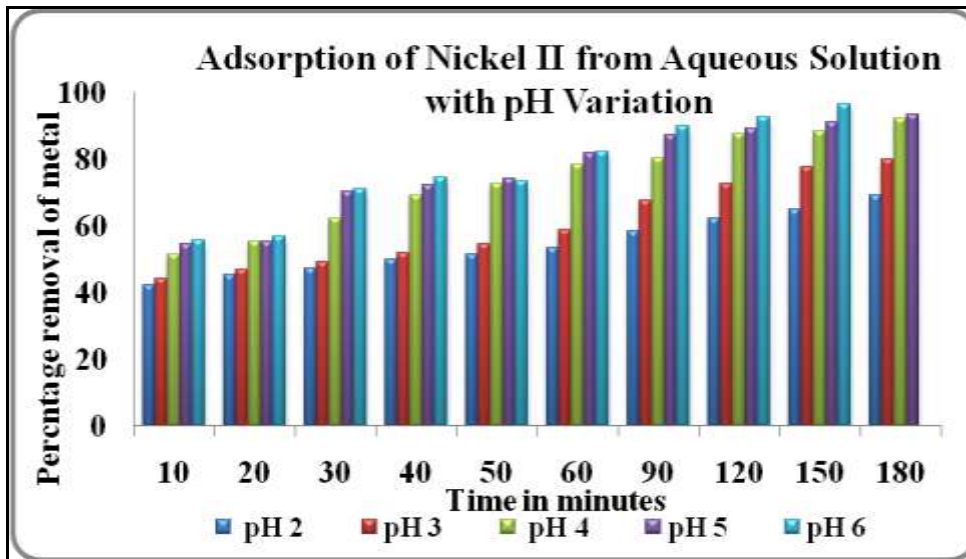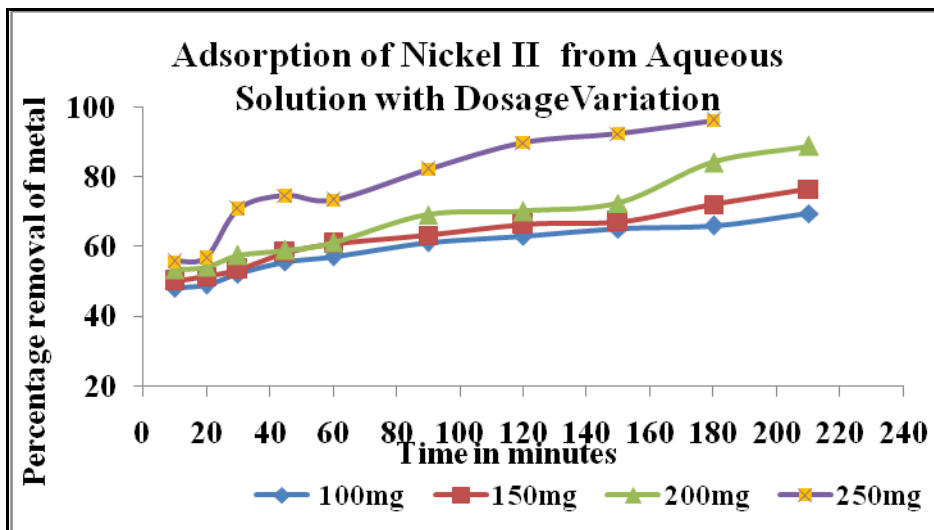
Figure 3

Figure.4

3.2.2 Effect of adsorbent dose

Adsorbent dosage is an important parameter that strongly influences the adsorption process by affecting the adsorption capacity of the adsorbent. The effect of adsorbent dosage is investigated for the removal of Ni(II) from aqueous solution by varying the dosage of the adsorbent CMAC from 100mg to 250mg. Batch mode experiment is carried out by using 100ml of metal solution containing 100mg metal/L at room 'T' and at pH 6.0 by varying the adsorbent dosage. It is observed that the percentage removal of metal ion increased, when the adsorbent dosage is varied from 100mg to 250mg (from 66.1% to 96.1%). The results obtained are graphically represented in Figure 4.The extent of adsorption depends on the available sites over the adsorbent. The adsorbent dose determine the number of active sites, and acts as an important parameter in adsorption for a given initial metal ion concentration.

The increase in the percentage removal of the metal ion with adsorbent dosage could be attributed to an increase in the surface area of the adsorbent, augmenting the more number of adsorption sites available for adsorption[14].

3.2.3 Effects of the initial concentration of Nickel (II) ion

The study of the distribution of the metal between the adsorbent and the metal ion solution at equilibrium is important to assess the adsorption capacity of the adsorbent for the Metal ion. The initial concentration of the metal solution is varied from 100 to 400 mg/l and batch mode experiment is performed at room "T' and at pH 3.0-7.0 to study the effect of initial concentration of metal solution on the removal of metal from aqueous solution and from Plating and Battery industrial effluent with 250mg of the adsorbent CMAC by varying the agitation time from 10 to 210 minutes.

The result obtained shows that the percentage removal of metals from aqueous solution used in this study decreases from 96.2% to 61.93% ,when the initial concentration of metal solution varied from 100 to 400 mg/l in 210 minutes of agitation time. The results are graphically depicted in Figure 5. Removal efficiency was higher for low concentration because of availability of unoccupied binding sites on the adsorbent. Removal efficiency decreased with increasing concentration because at high metal concentration the binding sites were almost completely covered.
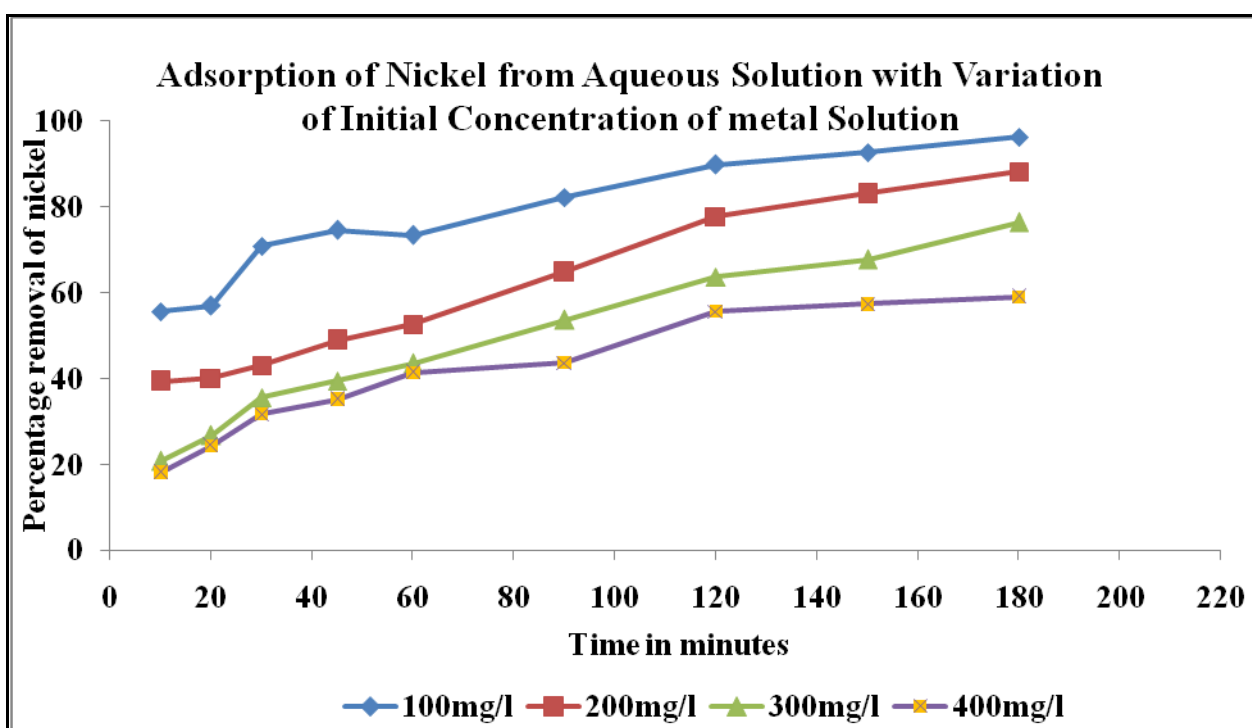

Figure. 5: Effect of initial concentration of Nickel (II) ion by CMAC

3.3 Adsorption isotherm

An adsorption isotherm model gives the equilibrium relationhip between the sorbate in the fluid phase (solution) and the sorbate sorbed on the sorbent at constant temperature[14,16]. They are very useful for obtaining the adsorption capacity so as to facilitate the evaluation of the feasibility of the adsorption process for a given application and for selection of the most appropriate sorbent at the optimum experimental condition[14].

In this work, adsorption isotherm was carried out at initial concentration of 100-400 mg/L. The Langmuir, Freundlich and Temkin isotherm models were employed to interpret the sorption process in order to understand the mechanism of Nickel (II) ion adsorption on CMAC. The Langmuir model shows the best fit with the highest correlation coefficient (r^2) values in the range of 0.9862 – 1.0, indicates the feasibility of the adsorption of the metal ion from aqueous solution using the adsorbent Cucumis Melopeel Activated Carbon, also suggest the monolayer coverage of the metal ion onto CMAC[17] and the homogeneous distribution of active sites on the surface of the adsorbent CMAC. The Freundlich adsorption isotherm plots are obtained by plotting log x/m vs log C_e for different concentration (100,200,300 and 400mg/L) of the metal solution. The plots obtained are linear shows the applicability of Freundlich adsorption isotherm for the removal of the metal ion from aqueous solution using CMAC as an adsorbent.

The Temkin isotherm[18] model contains a factor that explicitly takes into account the adsorbing species-adsorbate interaction. This model assumes the following facts: (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage[18,19], due to the adsorbent-adsorbate interaction, and then (ii) the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy.

The derivation in Temkin isotherm assumes that fall in the heat of adsorption is linear rather than logarithmic, as implied in Freundlich equation. The Temkin isotherm is applied in the following form

$q_e = RT/b \, [\ln(AC_e)]$
The linear form of Tempkin equation is
$q_e = \beta \ln \alpha + \beta \ln Ce$
where, $\beta = (RT)/b$,
T is the absolute temperature in Kelvin
R is the Universal gas constant, $8.314 \, J \, (mol \, K)^{-1}$
b is the Tempkin constant related to heat of sorption (J/mg)
A is the equilibrium constant corresponding to the maximum binding energy (L/g).

Table 1: Isotherm model parameters for the adsorption of Nickel by CMAC

Langmuir			Freundlich			Temkin		
r^2	$k_l{}^1$	R_L	r^2	K_f	$1/n$	r^2	β	b
0.999	1.003	0.90	0.966	0.370	0.159	0.9473	15.42	147.2

4. Conclusion

The present study was carried out to investigate the ability of Cucumis Melo peel in the removal of Nickel ion from aqueous solution. The results obtained showed that the equilibrium time for the adsorption of the ion onto adsorbent was 210 minutes. The data obtained fitted with Langmuir, Freundlich and Temkin isotherm model ($r^2 = 0.90$-0.999). The adsorption is highly influenced by parameters such as pH, adsorbent dosage and initial concentration of Ni^{2+}. The study has shown that Cucumis Melo peel which is abundantly available but generally considered of little or no value, has a considerable potential as an effective adsorbent for the removal of Nickel ion from aqueous solution. It can therefore have a place in the treatment of effluent from industries, thereby reducing the level of water pollution.

References

1. Bailey, R.A., Clark, H.M., Ferris, J.P., Krause, S., Strong, R.L., "Chemistry of the Environment", 2005, Academic Press, New York.
2. Parker, P., "Encyclopedia of Environmental Science" (2nd edn), 1980, Mc Graw Hill, New York, 354-358.
3. Namasivayam, C., Ranganathan, K., "Recycling of waste Fe(III)/Cr (III) hydroxide for the removal of Nickel from waste water adsorption and equilibrium studies", Waste Management., 1994,14, 709-716.
4. David, P., "Trace Element contamination of the Environment", 1977, Elsevier, Amsterdam", 11-43.
5. Smith, K.M., George, E.L., Stober, J. A., Feng, H.A., Kimmel, G.L., "Perinatal Toxicity Associated with Nickel Chloride Exposure".Environmental Research. 1993, 61, 200-211.
6. Hawash, S., Farash, J.Y., El-Geundi, M.S., "Investigation of Nickel ion removal by means of activated clay adsorption". Sci. Tech., 1994, 9, 244-257.
7. Kadirvelu, K., Thamaraiselvi, K., Namasivayam, C., "Removal of heavy metals from industrial waste waters by adsorption on to activated carbon prepared from agricultural solid waste". Bioresour. Tech., 2001, 76, 63-65.
8. Paramasivam, M., Namasivayam,C., "Removal of Ni(II) from aqueous solution and Nickel plating industry Waste water using an agricultural waste Peanut hull", Waste Management. 1995, 15, 63-68.

9. Viswakarma, P.P., Yadava, K.P., Singh, V.N., "Nickel(II) removal from aqueous solution by adsorption on to fly-ash, Pertankika", 1989, 12, 357 -366.

10. Bhattacharyya, K.G., Sarma, J., Sarma, A., "Azadirachta indica leaf powder as a biosorbent for Ni(II) in aqueous medium", Journal of Hazardous Materials, 2009, 165(1-3), 271-278.

11. Mas Rosemal H., Mas Haris, Kathiresan Sathasivam, "The removal of methyl red from aqueous solution using banana pseudostem fibers", American Journal of Applied Sciences, 2009, 6 (9), 1690-1700.

12. Demirbas, E., Kobya, M., Senturk, E., Ozkan, T., "Adsorption kinetics for the removal of chromium (VI) from aqueous solution on the activated carbons prepared from agricultural wastes". Water SA, 2004, 30: 533-539.

13. Givianrad,M.H., Rabani, M, Saber-Tehrani, M, Aberoomand-Azar, P., Hosseini Sabzevari, M., "Preparation and Characterization of nanocomposite, silica aerogel,activated carbon and its adsorption properties for Cd(II) ion from aqueous solution" Journal of Saudi Chemical Society, 2013, 17, 329-335.

14. Ahamed A. Jafar, Suganthana Balasubramanian, "Adsorption of Pb(II) Ion on Teak Leaves Activated Carbon- A Kinetic and Equilibrium Study" Pelagia Research Library Der Chemica Sinica, 2010, 1 (2): 35-43.

15. Ali Riza, D., Yalcin, G., Nusret, K., & Elcin, G., "Comparison of activated carbon and bottom ash for removal of reactive dye from aqueous solution", BioResour. Technol., 2007, 98, 834-839.

16. Binupriya, A. R., Sathishkumar, M., Jung, S. H., Song, S. H., & Yun, S. I., "A novel method in utilization of bok bunja seed wastes from wineries in liquid-phase sequestration of reactive blue", *Int. Jour. Environ, Res*., 2009, 3(1), 1-12.

17. Zheng, L., Dang, Z., Yi, Z. Zhang, H., "Equilibrium and kinetic studies of adsorption of Cd(II) from aqueous solution using modified corn stalk", J. Hazard. Mater. 2010, Vol. 176, pp. 650-656.

18. Temkin, M.J. Pyzhev, V., "Recent modification to Langmuir isotherms", Acta Physicochim, URSS, 1940, 12, 217-225.

19. Aharoni, C., Ungarish, M., "Kinetics of activated chemisorptions", Part 2. Theoretical models, J. Chem. Soc. Faraday Trans., 1977, 73,456–464.

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