

# Studies On Nickel (II) Ions Removal From Aqueous Solution By Using Citrus Aurantium L. Fruit Shells – A Low Costnanosorbent

S. Halimabi AliasShakilaBanu<sup>1</sup>, R. Sharmila<sup>2</sup>, G. Vijayakumar<sup>3</sup>

<sup>1,2</sup>Research scholar, PG & Research Department of chemistry, Arignar Anna Government Arts College, Musiri, Tiruchirappalli, Tamilnadu, India

<sup>3</sup>Assistant Professor, PG & Research Department of chemistry, Arignar Anna Government Arts College, Musiri, Tiruchirappalli, Tamilnadu, India

## ABSTRACT

Carbon materials are a class of significant and widely used engineering sorbents. As a new member of the carbon family, carbon nano-sorbents have exhibited great potentials in various applications especially the removal of pollutants from industrial wastewater. Therefore, the attempt has been made to study the removal of Ni(II) ions from aqueous solution using the nano-sorbent derived from Citrus aurantium L. fruit shells. The adsorption capacities are studied from adsorption isotherms such as Langmuir and Freundlich isotherms. The rate of sorption has proposed by the pseudo-first and second order kinetic models. The experimental results are correlated with FT-IR and SEM studies. The sorption capacity of Ni(II) ions are observed as very good in Citrus aurantium L. fruit shells nano-sorbent.

**Keywords:** Citrus aurantium L, Nickel, Isotherms, Kinetics and Nano sorbent

## I. INTRODUCTION

The source of nickel pollution is industrial processes such as connector, lead frame, tableware, plastics, manufacturing, electroplating, metal – finishing, nickel – cadmium batteries, fertilizers, pigments, mining and metallurgical operations. The presence of higher limits of nickel containing water arises the several health problems such as damage to lungs, kidneys, gastrointestinal distress, vomiting, pulmonary fibrosis, diarrhea, renal edema and skin dermatitis. Therefore, it is necessary to develop effective and inexpensive methods to removal of nickel. The nickel concentration wastewater has been reported up to 130 mg/L. It can approach 2 – 900 mg/L in plating rinse which is known to be one of the

major toxic pollutants [1]. In the present study various methods used by researchers to remove nickel from wastewater have been reported such as chemical precipitation, ion – exchange, chemical reduction, flocculation, filtration, solvent extraction, evaporation, adsorption, bio - adsorption, electro - dialysis and reverse osmosis. Among the above mentioned methods, adsorption method is very effective and low cost method for removal of heavy metals [2].

## II. MATERIALS AND METHODS

### 2. 1. Preparation of *Citrus aurantium* L.fruit shells Nano – sorbent (CANS)

Nano - sorbent is prepared from *Citrus aurantium* L. fruit shells nano – sorbent (CANS) which were locally procured. This material is simply dumped in the dust bin by the peoples. Therefore, it is low cost, economically and eco-friendly material that can used for removal of Ni(II) ions from aqueous solution. This material was collected from various juice shopping stalls and it was washed in hot distilled water to remove earthy matter, cut into small pieces and dried without direct sunlight. The precursors were impregnated in concentrated sulphuric acid (100g of material treated with 50ml of Con.H<sub>2</sub>SO<sub>4</sub>) for 24 hours. The charred material was washed with distilled water until the pH 7.0. Then the carbon was dried and activated at 400°C using muffle furnace. Finally it was ground and sieved. The sieved material was subject to the further grinding by using Ball milling process for 3 hours. Then, this final carbon powdered materials was used as annano – sorbent for removal of Ni (II) ions from aqueous solution.

## 2.2. Removal of Ni (II) Ions by Batch Equilibrium method

The adsorption experiments were carried out by batch equilibrium method. 100 mg of sorbent mixed with 100 mL of the adsorbate solution of desired concentration taken in the iodine flask and the mixture was agitated with different time intervals by using water-bath shaker with temperature controller at a constant speed of 175 rpm was used for adsorption studies. The solutions were centrifuged at regular time intervals and the residual concentration of Ni(II) ions present in the filtrate at each stage were determined using UV-Visible Spectrophotometer (Systronics 169, India). All experiments were carried out twice. The amount of Ni(II) ions adsorption was calculated from the difference of Ni(II) ions concentration in aqueous solution before and after adsorption [3].

The experimental variables were considered as follows,

- i. Initial concentration of metal ions range from 20 to 100 mg/L
- ii. Agitation time between sorbent and the metal ions solution from 5 to 40 min.
- iii. pH range from 1 to 8.
- iv. Dosage of the sorbent is 25 - 150 mg.
- v. Temperature range from 30°C to 50°C

Adsorption capacity is calculated using the following formula,

$$\text{Adsorption capacity } (q_e) = \frac{(C_0 - C_e) V}{W} \quad (2.2.1.)$$

$$\% \text{ of Removal} = \frac{(C_0 - C_e)}{C_0} 100 \quad (2.2.2)$$

where, C<sub>0</sub> = Initial concentration of metal ions (mg/L)

C<sub>e</sub> = Final concentration of metal ions (mg/L)

V = Volume of the metal ions solution (mL)

W = Weight of the sorbent (g).

## III. RESULTS AND DISCUSSION

### 1.1. Effect of Sorbent Dosage, pH and Agitation Time

These experiments are done by using 25mg to 150 mg of sorbents, 100ml of 100 mg/L of Ni(II) solution and agitation of various time intervals. The results indicate that the optimum dose is fixed as 100mg due to the quantity of Ni(II) uptake more [4], the optimum pH is fixed as 4 due to maximum removal of Ni(II) and the optimum agitation time is fixed as 30 minutes after this time removal of Ni(II) was constant [5].

### 1.2. Effect of Initial Concentration and Temperature

The equilibrium time was independent of initial Ni(II) concentration (C<sub>0</sub>). The results are shown below in **Table 3.1** revealed that, the amount of Ni(II)

adsorbed ( $q_e$ ) increases with the percentage removal slightly decreases while the increase in initial concentration of Ni(II) from 20 to 100 mg/L. This indicated that there exists a reduction in immediate solute adsorption owing to the lack of available active

sites on the sorbent surface, compared with the relatively large number of active sites required for the high initial concentration of Ni(II).

**Table 1.** Equilibrium parameters for the removal of Ni(II) by CANS

Initial conc. of Ni(II) ( $C_0$ ), mg/L	Equilibrium conc. of Ni(II) ( $C_e$ ), mg/L			Quantity of Ni(II) adsorbed at equilibrium ( $q_e$ ), mg/g			Ni(II) removal (%) by CANS		
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
	20	0.777	0.383	0.149	19.22	19.62	19.85	96.12	98.09
40	2.319	1.255	1.005	37.68	38.74	38.99	94.20	96.86	97.49
60	5.027	3.963	2.899	54.97	56.04	57.10	91.62	93.40	95.17
80	8.340	6.920	5.473	71.66	73.08	74.53	89.57	91.35	93.16
100	12.069	11.293	8.968	87.93	88.71	91.03	87.93	88.71	91.03

The percentage removal was dependent on initial concentration of Ni(II) solution and it increase, at a fixed concentration of Ni(II) with increase in temperature. This may be due to the increase in temperature; the rate of adsorption increased if the adsorption process is endothermic in nature. The increasing in adsorption with temperature may be due to the relative decrease in the escaping tendency of Ni(II) ions from the solid phase to the bulk phase[6].

**1.3. Adsorption Isotherms**

The adsorption equilibrium data presented in **Table 3.2 and Table 3.3** are described by the Langmuir and Freundlich isotherm models at three different temperatures are shown in the **Figure 3.1 and 3.2**. In Langmuir isotherm, the values of monolayer adsorption capacity ( $Q_0$ ) decreases with increase of temperature, suggesting that adsorption are favoured by lower temperature. This may be attributed to the fact that Ni(II) ions diffuse into sorbent at a slower rate with rise of adsorption system temperature. The energy of adsorption ( $b_L$ ) values suggests the affinities

of binding sites with the metal ions are favourable. The  $R_L$  values shown the range between 0 to 1 for the adsorption of Ni(II) at different concentrations which indicated the favorable adsorption of Ni(II) by CANS. These results indicated the efficiency of the sorbent is good under investigation [7].

In Freundlich isotherm, the values of adsorption capacity ( $k_f$ ) increases with increase in temperature of the solution from 30 to 50°C. It is shown that the adsorption is favoured at high temperature. The intensity of adsorption ( $n$ ) values are greater than unity signifies that the forces between the Ni(II) ions and sorbent surface are attractive which leads to the favourable adsorption and adsorption process is physical in nature. The equilibrium binding constant values and heat of adsorption values are shown to the minimum binding energy and minimum heat of adsorption during the adsorption of Ni(II) on CANS [8].

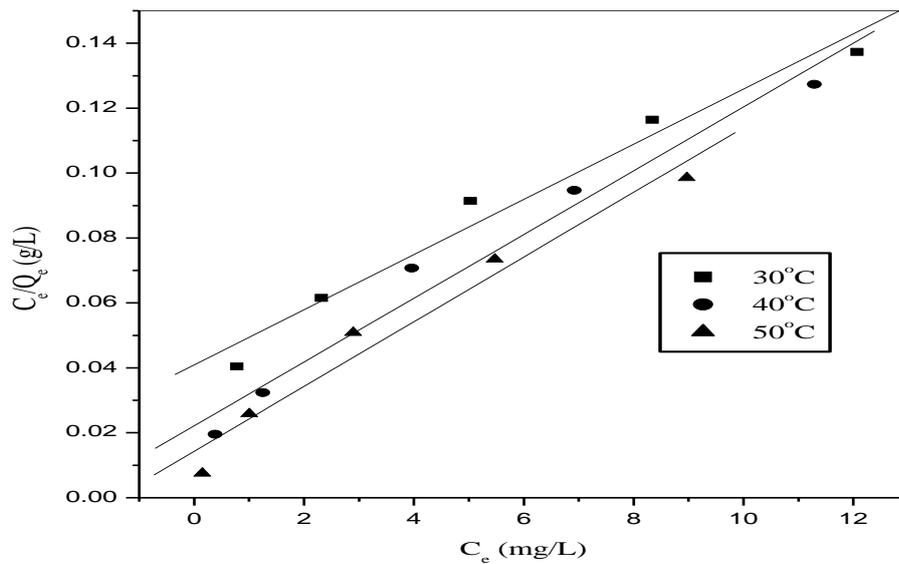
The goodness of fit of the experimental data is measured by the determination of correlation

coefficients. The correlation coefficients ( $r^2$ ) of Langmuir and Freundlich isotherm models and their constants are presented in **Table 3.2**. On comparing these two adsorption isotherm models, the linear form of Freundlich isotherm has high correlation coefficient values at all temperatures. Therefore, the

Freundlich model showed better fit than the Langmuir model and also it indicates that the metal adsorption by the sorbents was governed by physical adsorption.

**Table 2.** Results of isotherm models for the adsorption of Ni(II) on CANS

Temp. (°C)	Langmuir Isotherm			Freundlich Isotherm		
	Correlation coefficient	Constants		Correlation coefficient	Constants	
	$r^2$	$Q_0(\text{mg/g})$	$b_L(\text{L/mg})$	$r^2$	$k_f$	$n$
30	0.986	117.65	0.208	0.999	22.68	1.826
40	0.988	102.04	0.441	0.995	31.6	2.305
50	0.983	101.04	0.692	0.999	39.55	2.703



**Figure 1.** Langmuir isotherm for the adsorption of Ni (II) on CANS

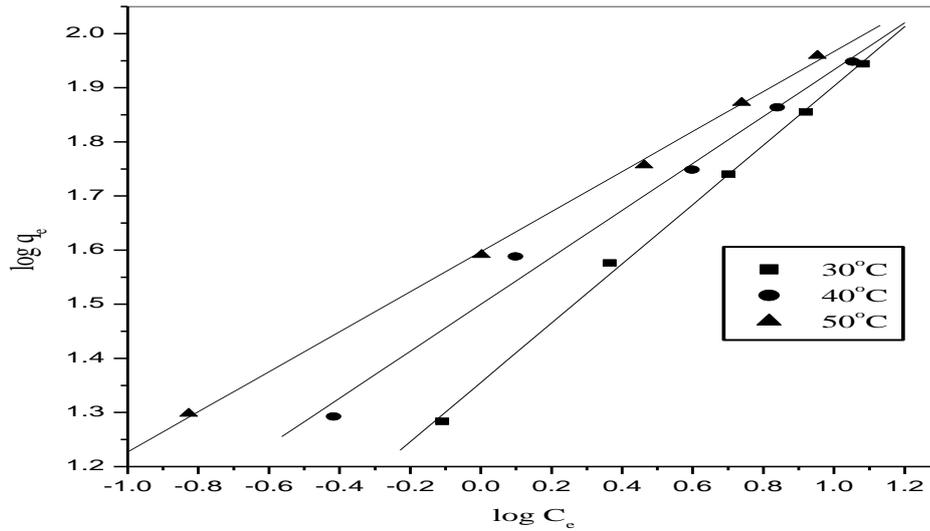


Figure 2. Freundlich isotherm for the adsorption of Ni(II) on CANS

### 3.5 Kinetics of Adsorption Studies

The pseudo-first order rate constant ( $k_1$ ), pseudo-second order rate constant ( $k_2$ ), percentage relative deviation ( $P$ ) and correlation coefficients ( $r^2$ ) are shown in the Table 3.4. The Figures 3.3 and 3.4 are shown the pseudo-first and pseudo-second order

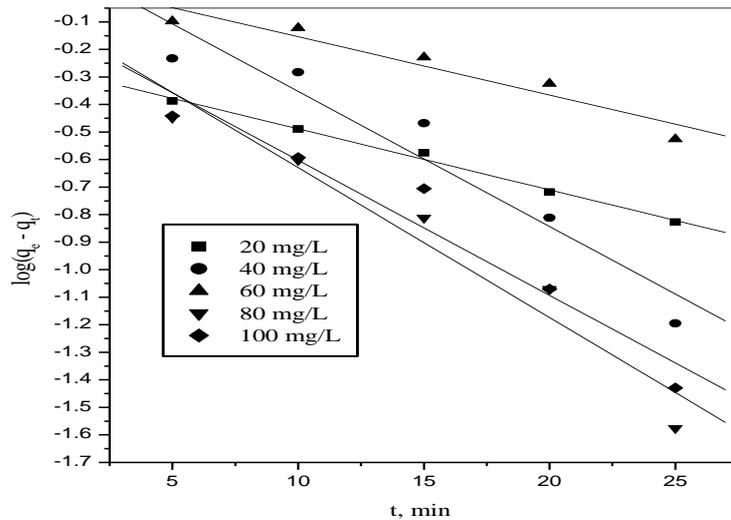
models for the sorption of Ni(II) from aqueous solution by CANS. A good agreement of sorption capacities between the calculated and experimental results were found in pseudo-second order model while comparing to pseudo-first order kinetic model.

Table 3. Pseudo-first and second order constants for the adsorption of Ni(II) on CANS

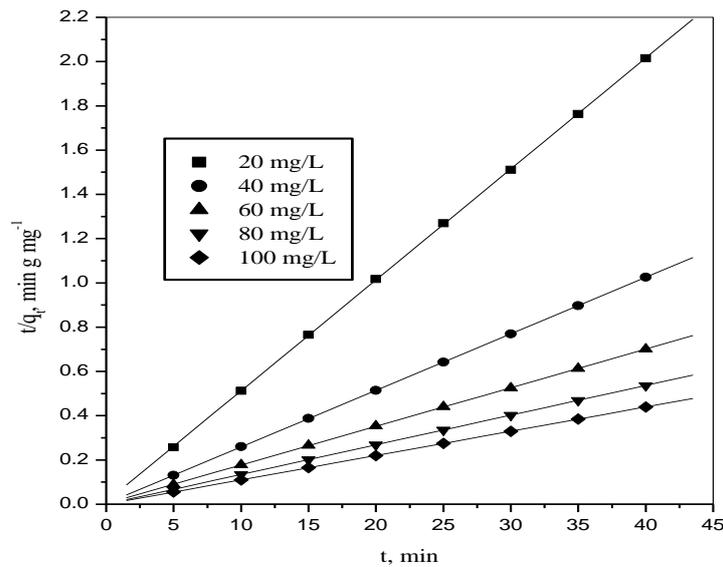
$C_o$ (mg/L)	$q_e(\text{exp})$ (mg/g)	pseudo-first order				pseudo-second order			
		kinetic model				kinetic model			
		$q_e(\text{cal})$ (mg/g)	$k_1$ ( $\text{min}^{-1}$ )	$r^2$	$P$	$q_e(\text{cal})$ (mg/g)	$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$r^2$	$P$
20	19.223	0.548	0.051	0.996	97.15	19.96	0.222	0.999	3.83
40	37.681	0.728	0.113	0.961	98.07	39.216	0.176	1	4.07
60	54.973	0.876	0.049	0.962	98.41	57.471	0.101	0.999	4.54
80	71.660	0.827	0.125	0.971	98.85	74.627	0.359	1	4.14
100	87.931	0.772	0.113	0.971	99.12	91.743	0.396	1	4.155

The experimental data obtained for the adsorption of Ni(II) with high correlation coefficient ( $r^2 = 1$ ) and very less percentage relative deviation in pseudo-second order model. From the above results, the pseudo-second order model was the best fit for the adsorption of Ni(II) than the pseudo-first order model. Many studies reported that the first order equation of Lagergren does not fit well to the adsorption process.

The first order kinetic model has been used for reversible reaction with an equilibrium being established between liquid and solid phases. Whereas, the pseudo-second order kinetic model assumes that the rate-limiting step may be physical adsorption. In many cases, the second order equation correlates well to the adsorption studies [10].



**Figure 3.** Pseudo-first order kinetic model for the adsorption of Ni(II) on CANS



**Figure 4.** Pseudo-second order kinetic model for the adsorption of Ni(II) on CANS

### 3.6 Fourier Transform Infrared Spectroscopic (FTIR)Studies

The FTIR spectra of CANS are taken before and after adsorption of Ni(II) ions and shown in figures 3.5 and 3.6. The FTIR spectrum of CANS before adsorption spectrum at 3842-3746  $\text{cm}^{-1}$  indicated the presence of -OH group of nano - sorbent. The peak at 3384  $\text{cm}^{-1}$  indicated the presence of N-H stretching. The aromatic -CH stretching observed at 2923  $\text{cm}^{-1}$ . A peak at 2759 -2678  $\text{cm}^{-1}$  indicated the presence of -CH stretching group of aldehydes. The region from 1608 - 1401  $\text{cm}^{-1}$  indicated the -C-C stretching of aromatic groups. The peak at 1100  $\text{cm}^{-1}$  indicated -CO stretching of alcohols group. After the adsorption of Ni(II) on CANS, there is a small shift in wave number and some of the wave number regions were not observed. This observation indicated the participation of adsorption of Ni(II) on CANS[11].

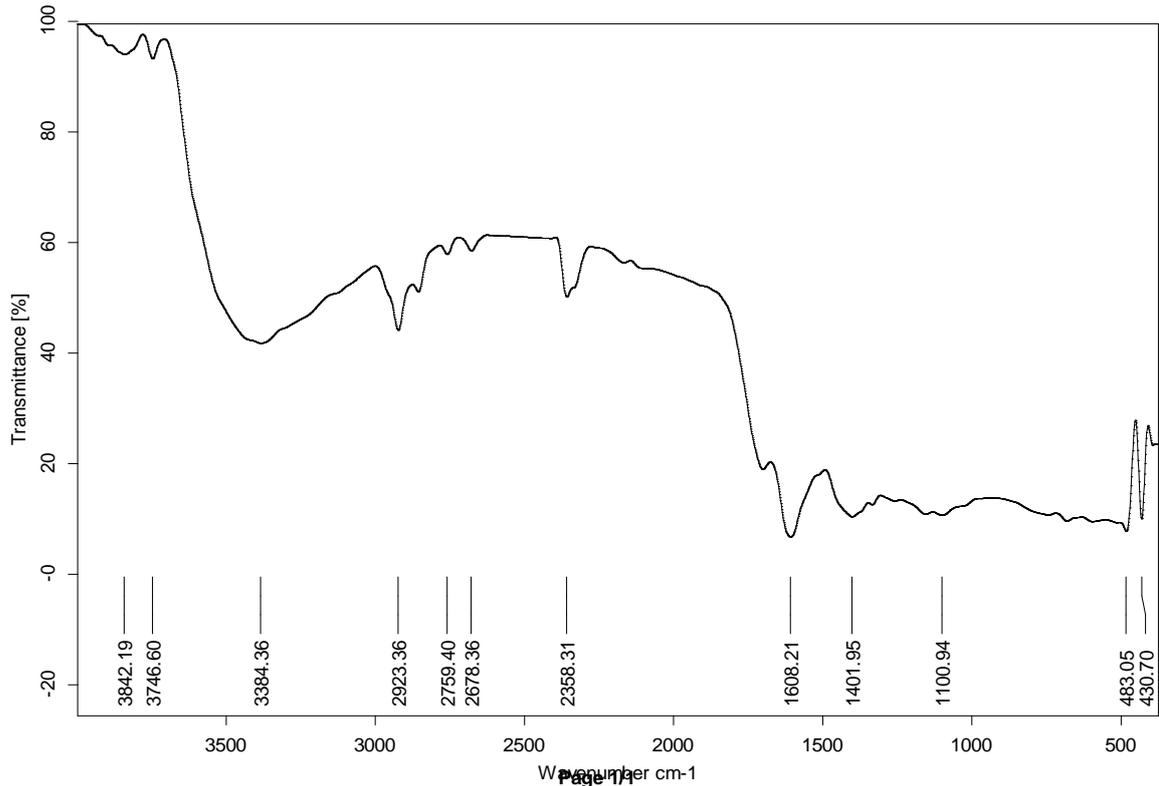
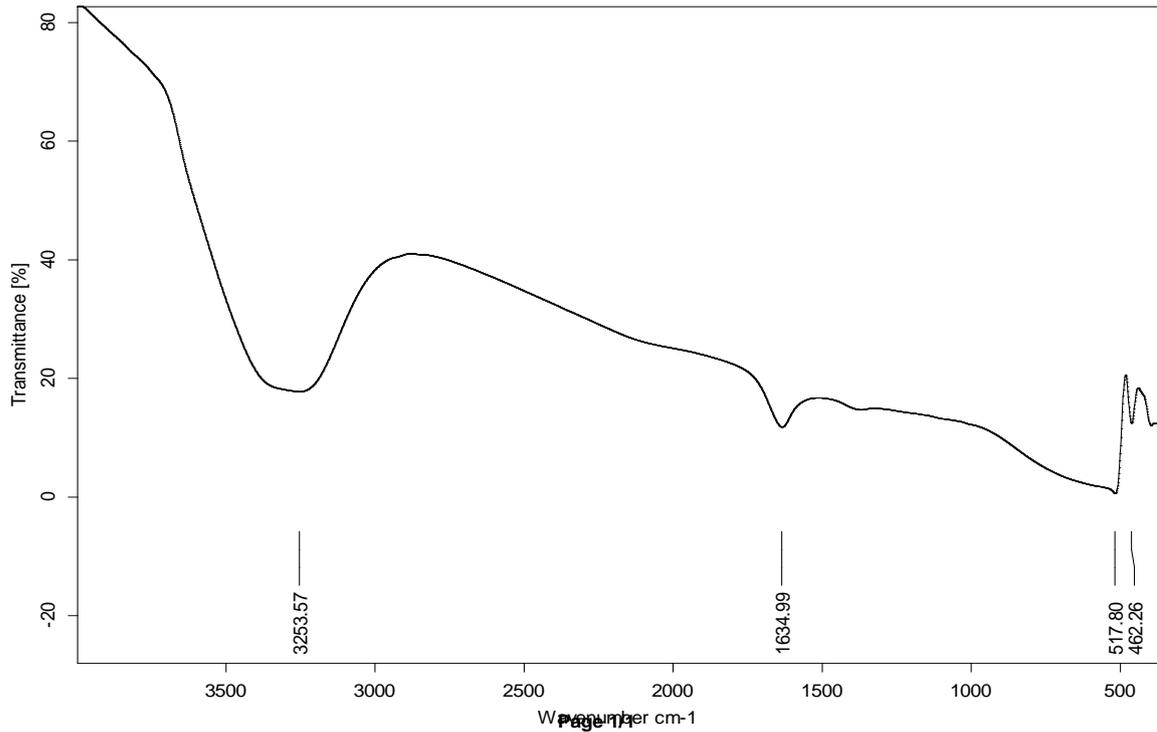


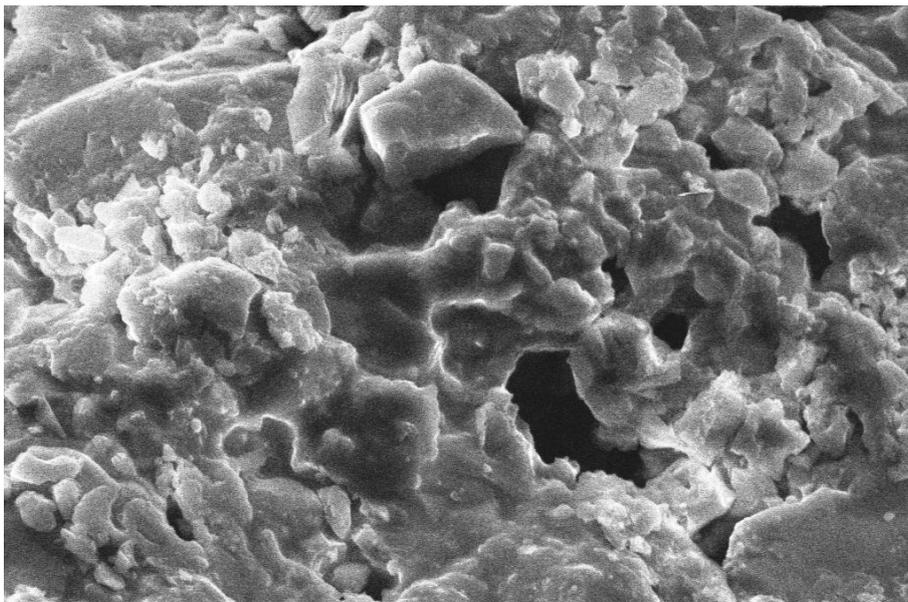
Figure 5. FTIR spectrum for CANS before adsorption of Ni(II)



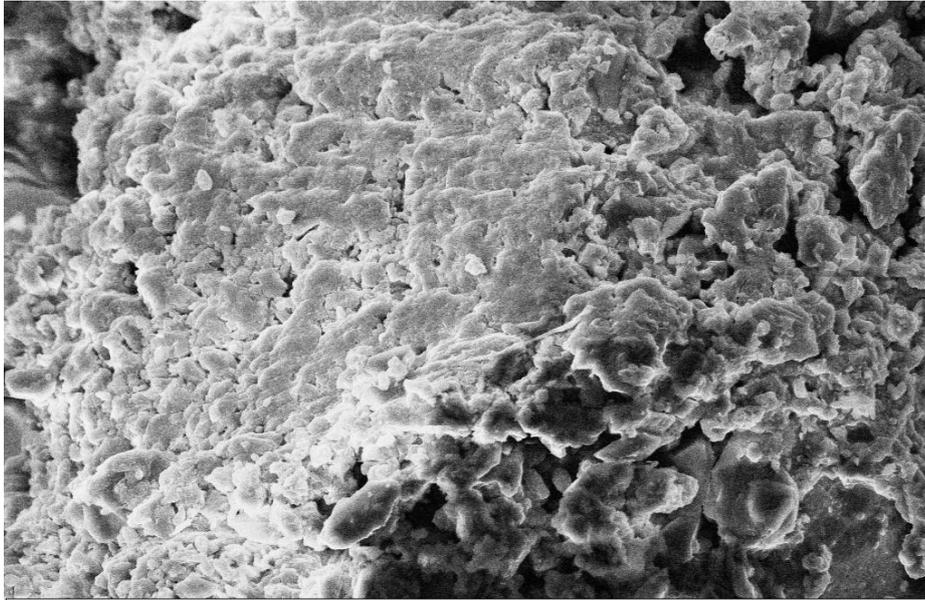
**Figure 6.** FTIR spectrum for CANS after adsorption of Ni(II)

### 3.7. Scanning Electron Microscope (SEM) Studies

The SEM photographs of CANS before and after adsorption are shown in the figures 3.7 and 3.8. It is clearly stated that the presence of porous structure of the nano - sorbent before adsorption. They have holes and cave type openings on the surface of the nano - sorbent which could definitely increase the surface area available for adsorption. After adsorption of Ni(II), SEM photographs are clearly seen that the surface of nano-sorbent were the caves, pores and surfaces of sorbents covered by Ni(II) ions. It is evident that the adsorbent structure is changed upon the adsorption of Ni(II) ions.



**Figure 7.** SEM photograph before adsorption of Ni(II) on CANS



**Figure 8.** SEM photograph after adsorption of Ni(II) on CANS

#### IV. CONCLUSION

Citrus aurantium L., fruit shells nano – sorbent (CANS) is abundant, environmental friendly and low cost material, could be used as a potential sorbent for the removal of Ni(II) from aqueous solution. The Freundlich adsorption isotherm model describes the adsorption behavior with good correlation coefficient than the Langmuir model. The optimum pH of the solution is 4, the optimum contact time is 30 minutes and adsorbent dosage is 100 mg used for the removal of Ni(II). It followed the pseudo-second order kinetic model. The percentage of removal of Ni(II) increased with increase the temperature from 30 to 50°C.

#### V. REFERENCES

- [1]. Sonali R. Dhokpande, Jayant P. Kaware and Sunil J. Kulkarni, "Research for removal of nickel from wastewater-A review", *Inter. J. sci., Engg and Tech. Res.*, Vol.2, No. 12, pp. 2162-2166, (2013).
- [2]. P. Muthusamy, S. Murugan and SmithaManothi, "Removal of nickel ion from industrial wastewater using maize cob", *ISCA J. of Biological Sci.*, Vol. 1, pp. 7-11, (2012).
- [3]. APHA, AWWA and WPCF. "Standard Methods for the Examination of water and waste water", 16th edition American Public Health Association, Washington, DC, pp. 445-456, (1985).
- [4]. LI. Onyeji and AA. Aboje, " Removal of heavy metals from dye effluent using activate carbon produced from Coconut shell", *Int. J. of Eng. Sci. Technol.*, Vol. 3, No. 12, pp. 8240-8243, (2011).
- [5]. ElifCaliskanSalihi, Jiabin Wang, Daniel J.L. Coleman and LidijaSiller, "Enhanced removal of Nickel(II) ions from aqueous solutions by SDS-functionalized grapheme oxide", *Sep. Sci. and Technol.*, Vol. 51, No. 8, pp. 1317-1327, (2016).
- [6]. V. Coman, B. Robotin and P. Ilea, "Nickel removal from industrial wastes-A review, *Resources, Conservation and Recycling*, Vol. 73, No. 229, (2013).
- [7]. I. Langmuir, *The constitution and fundamental properties of solids and liquids. Part I. J. Am. Chem. Soc.*, Vol. 38, No. 11, pp. 2221-2295, (1916).
- [8]. AM. El-Kamash, "Evaluation of zeolite-A for the sorptive removal of Cs<sup>+</sup> and Sr<sup>2+</sup> ions from aqueous solutions using batch and fixed bed

- column operations", *J. Hazard. Mater.*, Vol. 151, pp. 432-445, (2008).
- [9]. AshishGadhve and JyotsnaWaghmare, "Removal of heavy metal ions from wastewater by carbon nanotubes", *Inter. J. of chemical Sci. and Applications*, Vol. 5, No. 2, pp. 56-67, (2014).
- [10]. MehmetUgurlu, Ibrahim Kula, M. HamdiKaraoglu, and Y. Arslan, "Removal of Ni(II)ions from aqueous solutions using activated carbon prepared from olive stone by Zncl<sub>2</sub> activation". *Environ. Progress & Sustainable Energy*, Vol. 28, No. 4, pp. 547-557, (2009).
- [11]. ViboonSricharoenchaikul, ChiravootPechyen, DuangdaoAht-ong and D. Atong, "Preparation and characterization of activated carbon from the pyrolysis of Physic nut (*Jatropha curcas* L) waste", *J. Am. Chem. Soc.*, Vol. 22, No. 1, pp. 31-37, (2008).
- [12]. C. S. Lu, Y. L. Chung and K. F. Chang, "Adsorption thermodynamic and kinetic studies of trihalomethanes on multiwalled carbon nanotubes", *J. of Hazard. Mater.*, Vol. 138, pp. 304-310, (2006).