

Adsorption of Ni(II) from Synthetic Waste Water by Tea Waste Adsorbent

INDU SINGH¹, SHEEL RATAN² AND R. M. NAIK^{3*}

Department of Chemistry, University of Lucknow,
Lucknow-226007, India, E-mail: radheynaik@gmail.com

Abstract

In this work, a low cost adsorbent was prepared from tea waste and it was used for the removal of Ni(II) ions from its aqueous solution. Different variable conditions such as pH, initial metal ion concentration, adsorbent dose, contact time, and temperature were include for find out the adsorption capacity of adsorbent. SEM, FTIR, and BET analysis were used to characterize the adsorbent. The data obtained from experiments were analyzed by using the Langmuir and Freundlich Isotherms. The results showed that the tea waste can be utilized as a low-cost adsorbent for the removal of Ni(II) ions from its aqueous solution. The strong choice to use tea waste as an adsorbent is due to find out the economic way of metal removal. Experimental results showed that maximum removal of Nickel ion by tea waste is 85% respectively at optimum condition.

Keywords: Adsorption, Ni(II), tea waste, isotherms, kinetics.

Introduction

The term heavy metal is collectively applied to a group of metals with density greater than 5g/cm³ [1]. Electroplating, battery manufactures, painting, paper, pigments, fuels, photographic materials, explosive manufacturing and metal working industries discharge large amounts of heavy metal in their effluent [2]. Heavy metals are major pollutants in the environment due to their toxic, biodegradable and carcinogenic nature [3]. The effects of Ni exposure vary from skin irritation to damage of the lungs, nervous system, and mucous membranes [4] neurological signs and increased thirst [5]. Several processing techniques are available to reduce the concentrations of heavy metals in wastewater, including precipitation, flotation, ion exchange, solvent extraction, and adsorption [6]. Adsorption is one of the alternatives for such causes the tendency of molecules from an ambient fluid Phase to adhere to the surface of a solid [7]. It has advantages over other methods are the simple design, sludge-free and can involve low investment in terms of both the initial costs and land [8]. Adsorption onto activated carbon is a well-known method for removing toxic metal ions, but the high cost of activated carbon restricts its use in developing countries [9]. The adsorption abilities of a number of low cost adsorbents (Tea waste, agriculture waste and biomass) have been determined for the removal of heavy metals from water [10]. Therefore, there is a need to look into alternatives to investigate a low-cost adsorbent which is effective and economic, for potential approach is the use of tea waste, Tea is one of the most popular beverages and about 3.5 million tons of tea was consumed annually in the world [11] and in India yearly production of tea is approximately 857000 tonnes which is 27.4% of total world production [12], the amount of dry tea produced from 100 kg green tea leaves is 22 kg on average and approximately 18 kg tea is packed for the market. The other 4 kg of dry tea material is wasted [13]. Amount of TW produced per year after processing is about 190400 tonnes in India alone, very few investigators have investigated TW as an adsorbent for the removal of heavy metals. In last few years, a vast number of publications have been

dedicated to the removal of heavy metals from waste water by using adsorption techniques with different low cost materials, in recent years, tea waste (TW) is also gaining grounds due to its potential to overcome heavy metal pollutants. Insoluble cell walls of tea leaves are largely made up of cellulose and hemicelluloses, lignin, condensed tannins and structural proteins [14, 15]. In this investigation experiment perform to evaluate the effectiveness of employing a tea waste for the adsorptive removal of Ni from synthetic waste water, using batch experiment and isotherm studies to determine the adsorption capacities.

Nickel

Environmental contamination due to Nickel, electroplating is one important process involved in surface finishing and metal deposition for better life of articles and for decoration. Although several metals can be used for electroplating, nickel, copper, zinc and chromium are the most commonly used metals, the choice depending upon the specific requirement of the articles [16], during washing of the electroplating tanks, considerable amounts of the metal ions find their way into the effluent. Ni (II) is also present in the effluents of silver refineries, zinc base casting and storage battery industries etc [17]. Its enter in the food chain progressively larger accumulation of nickel compounds takes place in humans and animals, higher concentration of nickel causes cancer of lungs, nose and bone [18], Dermatitis is the most frequent effect of exposure to Ni, acute poisoning of Ni (II) causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness [19].

Materials and methods

Adsorbent preparation

Tea waste collected from tea stalls and restaurants were washed and boiled with hot distilled water (85°C) up to colour removal. After colour removal it is dried in hot oven at 105°C for 12 hours. The dried material converted into powder form by mixer grinder and screened to size 100 µm. This powder was carbonised in muffle furnace at 150 °C for 2 hours and then stored in plastic bags at room temperature. Carbonized material converted into powder form by mixer grinder and screened to size 100 µm. Carbonized tea waste washed again by double distilled water and then dried in air oven at 105 °C. This carbonized, washed and dried tea waste was packed in air tight container for further use.

Batch mode adsorption studies

To prepare synthetic stock solution (1000mg/L) of Ni(II), calculated quantity of NiSO₄.6H₂O was added double distilled water. The standard solutions were made by diluting the stock solution. All other chemical used, were analytical grade. The adsorption of heavy metals on tea waste was studied by batch technique by shaking 2g adsorbent with 50 ml of Ni(II) aqueous solution of known concentration (10-100mg/L) at a fixed temperature (30 °C) in a orbital shaker for a known period (120 Min.) of time. After equilibration, the suspension of the adsorbent was separated from solution by filtration using Whatman No. 1 filter paper .The concentration of heavy metal ions remaining in solution was measured spectrophotometrically. The effect of several parameters, such as pH, concentrations, contact time and adsorbent dose on the adsorption was studied. The pH of the adsorptive solutions was adjusted using hydrochloric acid and sodium hydroxide. The results of these studies were used to obtain the optimum

conditions for maximum heavy metals removal from aqueous solution. The percentage removal of heavy metal and amount adsorbed per unit mass was calculated using Eqs. (1) & (2) respectively [20].

$$\% \text{ Removal of metal ions} = \frac{(C_0 - C_e)V}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

Where: C_0 is the initial metal ion concentration of test solution in mg/L, C_e is the final equilibrium concentration of test solution in mg/L and V is the amount of the metal ion solution in L.

Results and discussion

Characterizations of adsorbent

The Fourier transform infrared spectroscopy (FT-IR) spectra of after and before adsorption on adsorbent prepared from tea waste is shown in Figure 1. The change in peaks shows the adsorption on adsorbent surface. The morphology of surface is shown in Figure 2 with the help of Scanning Electron Microscopy (SEM) image.

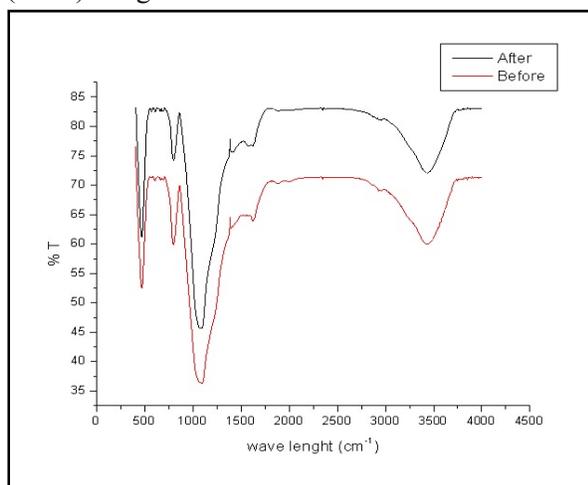


Figure 1: FTIR Spectrum of tea waste after and before adsorption

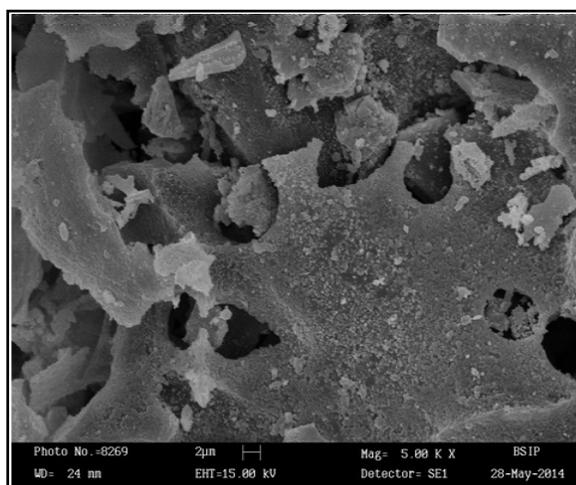


Figure 2: SEM image of tea waste

Effect of contact time

The variation in the percentage removal of heavy metals with contact time using 2 g/50ml of tea waste adsorbent at pH 6.0 for varying contact time 0-3 hours. It is observed that, the percentage removal of Ni (II) ions is nearly 91% at equilibrium. With increasing contact time up to 120 min, removal efficiencies increase very fast, Fig. 3. Maximum removal obtained at 180 minutes. The optimal contact time to attain equilibrium with tea waste adsorbent is 120 minutes in all other experiments.

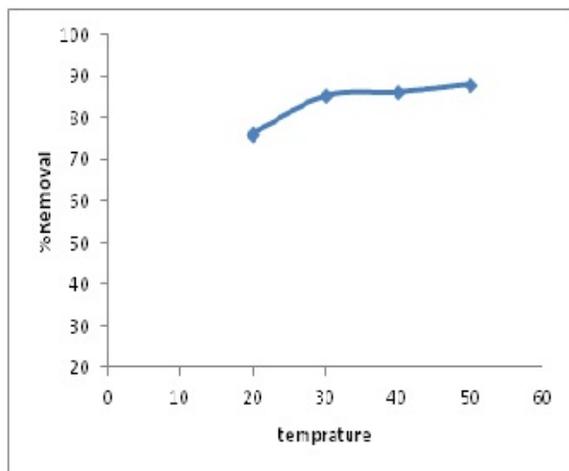


Figure 3: Effect of Contact Time

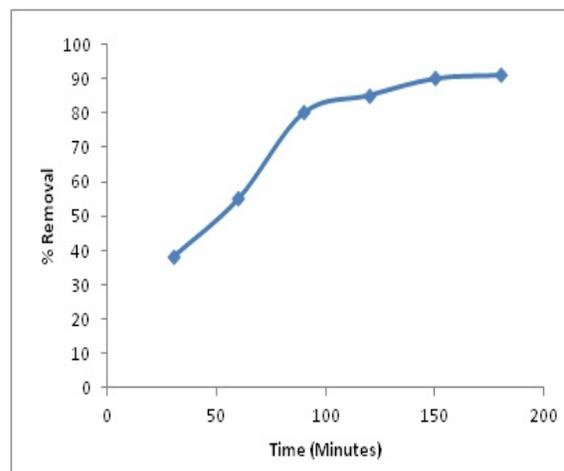


Figure 4: Effect of Temperature

Effect of temperature

The uptake of Ni(II) by activated tea waste at different temperatures (20-50 °C) was shown in Fig. 4. The result demonstrated that the uptake capacity increases with increase in temperature and thus confirms the endothermic nature of adsorption process. The enhancement in uptake is attributed to better interaction between metal ions and adsorbent, creation of new adsorption sites and increased intraparticle diffusion at higher temperatures [21]. The uptake increased from 38.09 to 44.06 mg/g when the temperature increased from 20 to 50 °C. Other studies have reported similar observations regarding the effect of temperature on adsorption capacity [22].

Effect of pH

Variation of pH is one of the most important parameters controlling uptake of metals from aqueous solutions. Figure 5 shows the effect of pH range 2-8 on heavy metals removal efficiencies of tea waste adsorbent. These studies were conducted at an initial metal ions concentration of 50gm/L in 50ml solution, adsorbent dose 2 g/50ml solution and contact time 120 minutes. The percentage adsorption increases with pH to attain a maximum at pH 6.0 and thereafter it decreases with further increase in pH. The maximum removals of Ni (II) at pH 6.0 were found to be nearly 85.28%. This may be due to the partial hydrolysis of M^+ resulting in the formation of MOH and $M(OH)_2$. With increase of pH from 2 to 6, the metal exists as $M(OH)_2$ in the medium and surface protonation of adsorbent is minimum, leading to the enhancement of metal adsorption[23]. Increase in OH^- ions cause a decrease in adsorption of metal ions at adsorbent-adsorbate interface. Lower solubility of hydrolysed metal ions species may be another reason for the maximum adsorption at pH 6.0. Since, in lower pH range, metal is present predominantly as metal ions in the adsorptive solution, there is a competition between H^+ and M^+ ions for adsorption at the ion exchangeable sites, leading to a low removal of metal [24-25].

Effect of adsorbent dose

The results for adsorptive removal of heavy metals with respect to adsorbent dose are shown in Figure 6, over the range 0.25 to 5gram/50ml, at pH 6 and 120 minutes contact time. It is observed that there is a sharp increase in percentage removal of Ni(II) with increase in adsorbent dose, maximum removal of Ni(II) is 89.55% at 2gram adsorbent dose. It is apparent that the percent removal of heavy metals

increases rapidly with increase in the dose of the adsorbents due to the greater availability of the exchangeable sites or surface area.

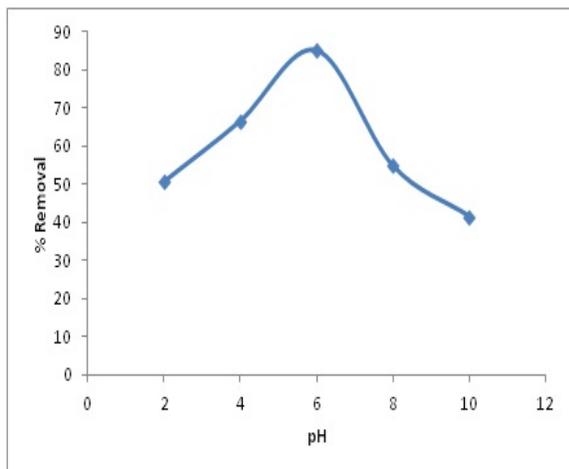


Figure 5: Effect of pH

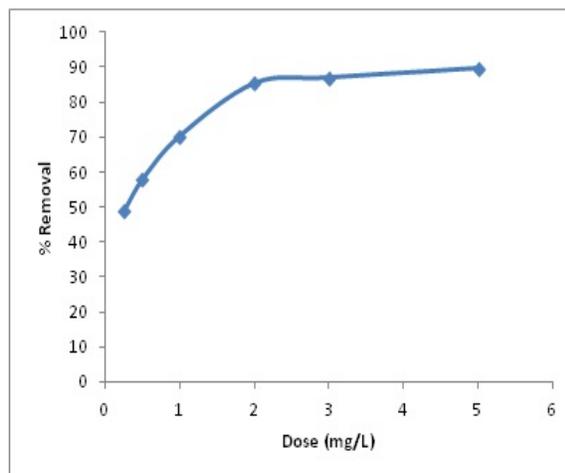


Figure 6: Effect of adsorbent dose

Effect of initial concentration of heavy metal

The effect of concentration was observed at 2g/50ml adsorbent dose, pH 6.0, and 120 minutes of contact time, shown in Figure 5. The percentage removal of metal ions by tea waste adsorbent, decreases with the increase in initial metal ion concentration. For Ni (II) the percentage removal is highly effective on the 10mg/L of initial concentration after which percentage removal decreases gradually. At lower initial metal ion concentrations, sufficient adsorption sites are available for adsorption of the heavy metals ions. Therefore, the fractional adsorption is independent of initial metal ion concentration. However, at higher concentrations the numbers of heavy metal ions are relatively higher compared to availability of adsorption sites. Hence, the percent removal of heavy metals depends on the initial metal ions concentration and decreases with increase in initial metal ion concentration [26].

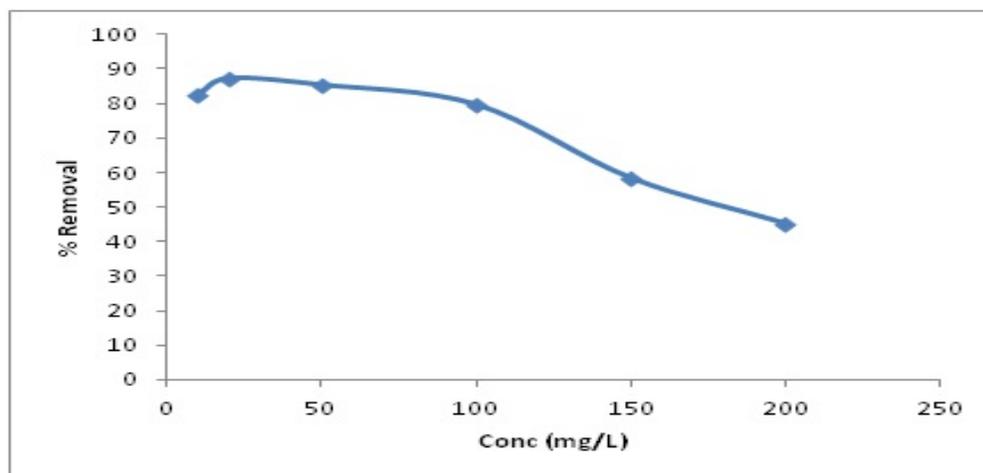


Figure 7: Effect of initial metal ion concentration

Adsorption isotherms

Two isotherms (Langmuir and Freundlich) were used to explain the experimental data. Results show that Langmuir isotherm is better fit to experimental data. The constant of Langmuir and Freundlich are shown in Table No.1.

Freundlich Adsorption Isotherm

The adsorption data of Ni(II) ions onto carbonized and activated tea waste was apply to Freundlich isotherm, in the following linear form:-

$$\text{Log } q_e = \text{Log } K_f + (1/n) \text{Log } C_e \quad (3)$$

Where, q_e is the amount of metal ion adsorbed per gram of adsorbent (mg/g). C_e is the equilibrium concentration of metal ion in solution (mg/L). K and b are Freundlich constants, indicating the Adsorption Capacity and Adsorption Intensity respectively. The K_f and n values were calculated from intercept and slop of the plot respectively and presented in Table 1. The Correlation coefficient $R^2= 0.857$.

Langmuir Adsorption isotherm

The Langmuir isotherm is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface.

The Linear form of Langmuir equation is

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (4)$$

q_{\max} and K_L is Langmuir Constants related to the capacity and energy of sorption respectively. The values of q_{\max} and K_L and Correlation coefficient obtained from the Langmuir model are shown in Table 1. The Correlation coefficient $R^2 = 0.99$ suggests that adsorption of Ni(II) ions onto Carbonized and activated tea waste follows the Langmuir isotherm. The maximum monolayer capacity q_{\max} obtained from the Langmuir is 4.177 mg/g.

Table-2 Kinetic model value for adsorption of

Table-1 Adsorption Isotherm

Ni(II) onto carbonized and activated tea waste

Freundlich Constants			Langmuir Constants		
K_F	n	R^2	K_L	q_{\max}	R^2
1.99	1.8329	0.86	12.2143	4.177	0.99

Pseudo first order kinetics		Pseudo second order kinetics	
k_1	R^2	k_2	R^2
0.0327	0.95	1.06×10^{-8}	0.98

Adsorption kinetics

The rate of adsorption of Ni(II) on carbonized and activated tea waste was studied by using the pseudo first order kinetic model and Pseudo second order kinetic model to test the experimental data.

Pseudo first order kinetics

The rate of adsorption of Ni(II) on carbonized and activated tea waste was studied by using the pseudo first order rate equation proposed by Lagergren, Eq 5. It is found that as initial Ni(II) concentration increases, Lagergren rate constant decrease. This indicates that, adsorption does not follow the 1st order kinetics.

$$\text{Log}(q_e - q_t) = \text{Log} q_e - \left(\frac{k_1 t}{2.303} \right) \quad (5)$$

Pseudo Second order models

The time data of metal ion fitted to Pseudo second order kinetics, Eq 6. Pseudo second order model showed that, Rate constant k_2 is almost constant at different initial concentration which is shown in Table 2. This indicates that adsorption of Ni(II) carbonized and activated tea waste was studied obey the 2nd order kinetics.

$$\frac{t}{q_t} = \frac{1}{k_2 q_1^2} + \frac{1}{q_1} t \quad (6)$$

Conclusions

Tea waste is a cheap and effective adsorbent for the removal of Ni(II) ions from waste water without requiring any pre-treatment. Experiment results showed that maximum removal of Nickel ion by tea waste at optimum condition (pH 6.0, 120 minutes of contact time, 2g/50ml of adsorbent dose and 50mg/L of initial metal ion concentration) is 85.28%. The experimental studies show that the tea waste would be quite useful as an adsorbent for the removal of heavy metal ions from contaminated industrial effluents due to easy availability and economically.

References

- [1] H. Mahavi, D. Naghipour, F. Vaezi and S. Nazmara, "Teawaste as an adsorbent for heavy metal removal from industrial wastewaters" American J. App. Sci., 2 (1), pp 372-375, (2005).
- [2] M. Oteroa, F. Rozada, A. Morán, L. F. Calvo, A. I. García, "Removal of heavy metals from aqueous solution by sewage sludge based sorbents" competitive effects, Desalination 239, pp 46–57, (2009).
- [3] S. J. Banum, "Introduction to Organic and Biological Chemistry, third ed" Macmillan Publishing Co., New York, NY, p. 541, (1982).
- [4] M. N. Khan, M. F. Wahab, "Characterization of chemically modified corncobs and its application in the removal of metal ions from aqueous solution" J. Hazard Mater. B141, pp 237–244, (2006).
- [5] Y. Liu, Cao, Luo, Q., F., J., Chen, "Biosorption of Cd²⁺, Cu²⁺, Ni²⁺ and Zn²⁺ ions from aqueous solutions by pretreated biomass of brown algae" J. Hazard. Mater. 163, pp 931–938, (2009).
- [6] Boonamnuayvitaya, W. Chaiya, S. Tanthapanichakoon, Jarudilokkul, "Removal of heavymetals by adsorbent prepared from pyrolyzed coffee residues and clay" Sep. Purif. Technol. 35, pp 11–22, (2004).
- [7] R. Jalali, H. Ghaofurian, Y. Asef, S. J. Davarpanah, S. Sepehr "Removal and recovery of lead using non-living biomass of marine algae" J. Hazard. Mater. B 92, pp 253–262, (2002).
- [8] S. B. Wang, M. Soudi, L. Li, Z. H. Zhu, "Coal ash conversion into effective adsorbents for removal of heavy metal and dyes from wastewater" J. Hazard. Mater. 133pp 243 251, (2006).
- [9] E. Malkoc, Y. Nuhoglu, "Investigations of Nickel (II) Removal from Aqueous Solutions Using Tea Factory Waste" J. Hazardous Materials, B127, pp 120, (2006).
- [10] N., Kuyucak, B., Volesky "Biosorbent for recovery of metals from industrial solutions" Biotechnol. Lett. 10, pp 137–142, (1998).
- [11] A. H. Mahavi, D. Naghipour, F. Vaezi and S. Nazmara, "Teawaste as an adsorbent for heavymetal removal from industrial wastewaters" American J. App. Sci., 2(1), pp 372-375, (2005).

- [12] R. Jalali, H. Ghafourian, Y Asef, S. J. Davarpanah, S. Sepehr, "Removal and recovery of lead using non-living biomass of marine algae" *J. Hazard. Mater. B* 92, pp 253–262, (2002).
- [13] S. Babel, T. A Kurniawan, "Low-cost adsorbents for heavy metals uptake from contaminated water: a review" *J. Hazard. Mater.* 97, pp 219–243, (2003).
- [14] U. Soffiotti, J. K Wagoner, "Occupational Carcenogenesis" *New York Academy of Science*, pp 271, (1976).
- [15] M. Sitting, "Toxic Metals—Pollution Control and Worker Protection" *Noyes Data Corporation*, New Jersey, (1976).
- [16] P. Parker, "Encyclopaedia of Environmental Science, second ed" *Mc- Graw Hill*, New York, (1980).
- [17] A. Lopez-Delgado, C. Perez, F. A. Lopez, "Sorption of heavy metals on blast furnace sludge" *Water Res.* 32 pp 989–996, (1998).
- [18] M. O. Corupcioglu, C. P. Huang "The adsorption of heavy metals onto hydrous activated carbon" *J. Water Res.* 21, pp 1031 (1987).
- [19] R. P. Beliles, "The lesser metals in: F.W. Oehme (Ed.), *Toxicity of Heavy Metals in the Environment*" Part 2, *Marcel Dekker*, New York, p. 383 (1979).
- [20] D. C. Barrell, "Atomic Spectrophotometer Analysis of Heavy Metals Pollutants in Water" *Ann Arbor Science Publishers Inc.*, Ann Arbor, MI, pp. 25 (1975).
- [21] S. J. Banum, "Introduction to Organic and Biological Chemistry" third ed., *Macmillan Publishing Co.*, New York, pp 541 (1982).
- [22] S. Babel, T. A. Kurniawan "Low-cost adsorbents for heavy metals uptake from contaminated water: a review" *J. Hazard. Mater.* 97, pp 219–243 (2003).
- [23] S. J. Gregg, K. S. W. Sing "Adsorption, Surface Area and Porosity", *Academic Press*, New York (1982).
- [24] A. H. Mahavi, D. Naghipour, F. Vaezi and S. Nazmara."Tea waste as an adsorbent for heavy metal removal from industrial wastewaters" *American J. App. Sci.*; 2(1) pp 372-375 (2005).
- [25] E. Malkoc, Y. Nuhoglu, "Investigations of Nickel (II) Removal from Aqueous Solutions Using Tea Factory Waste", *J. Hazardous Materials*, B127, pp 120 (2005).
- [26] E. Malkoc and Y. Nuhoglu Removal of Ni(II) ions from aqueous solutions using waste of tea factory: adsorption on a fixed-bed column" *J. Hazardous Materials*; B135 pp 328-236 (2006b).
- [27] A. H. Hawari and C. N. Mulliga, Biosorption of lead(II), cadmium(II), copper(II) and nickel(II) by anaerobic granular biomass. *Bioresour. Technol.*; 97(4) pp 692-700, (2006).
- [28] P. X. Sheng, Y. P. Ting, J. P. Chen, L. Hong. "Sorption of lead, copper, zinc and nickel by marine algal biomass: chracterization of biosorptive capacity and investigation of mechanisms" *J. Colloid Interface Sci.* 275, pp 131-141, (2004).