

Chapter III

Experimental Section

3.1 Identification of Adsorbent Materials

On the basis of thorough investigation of the literature studies, two potential materials, their origin being agricultural and marine based viz., *Pistachio vera* shells and Bivalve shells have been identified for their employability in the chelation of selected toxic metal ions and anions. These eco-safe green materials are biocompatible, biodegradable, nontoxic, economically viable, abundant, indigenous, safe to handle with appreciable regeneration capacity.

3.2 *Pistachio vera* Shell

Pistachio vera (*Pistacia vera* L), being the only edible crop of 11 species in the genus *Pistachia* is one of the popular nuts. Pistachio is a desert plant, highly tolerant of saline soil. It grows upto 10 m (33 ft) tall. *Pistachio vera* Shell (PVS) is the main by-product of commercial pistachio processing, constituting approximately 37% of the dried pistachio drupe¹. The hard, cream-colored exterior shells considered as litter without any commercial value were collected from various localities in Coimbatore, Tamil Nadu, India.

3.3 Bivalve Shell

Pear-shaped, bivalves belong to the marine family *Mytilidae*, most of which live on exposed shores in the intertidal zone, attached by means of their strong abysal threads to a firm substrate. These molluscs are from brackish/ freshwater habitats. The middle prismatic layer of the shell is composed of crystalline calcium carbonate and the innermost nacreous layer consists of thin layers of calcium carbonate². These Bivalve shells (BVS) were collected from sea shores in and around Kerala. The composition of the selected materials are listed in Table 3.1

Table 3.1 *Pistachio vera* and Bivalve Shells Composition

<i>Pistachio vera</i> Shell		Bivalve Shell	
Component	Composition (%)	Component	Composition (%)
Protein	19.3	Protein	9.99
Mineral	2.9	Mineral	51.62
Lipids	53.7	Chitin	23.25
Carbohydrate	19	Chitosan	15.14

3.4 Assortment of Chosen Materials

The collected materials were cleaned carefully and dried under the sunlight for a period of ten days. The dried materials were then pulverized using electrical mixer and categorized into various mesh sizes viz., 85 BSS, 72 BSS, 52 BSS, 36 BSS and 22 BSS with scientific test molecular sieves. The pictorial representations of collected materials (PVS, BVS) and their sieved powders (PVSP, BVSP) are shown in the figure 3.1

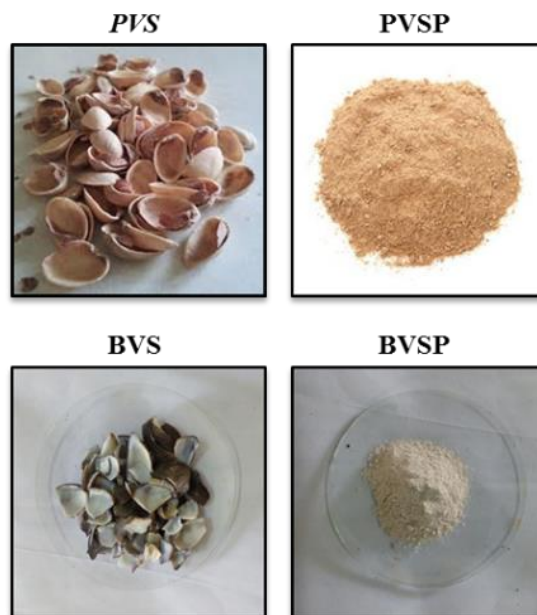


Figure 3.1 *Pistachio vera* shell / Bivalve shell images

3.5 Choice of Metal ions/ Anion

The sorbate species probed for the present study include: Lead [Pb(II)] / Nickel [Ni(II)] and Phosphate [PO_4^{3-}] ions, based on indepth survey carried out in and around Coimbatore, where industries, notoriously discharging these species as effluents were identified. The ubiquitous solid wastes/ metals and anions are being dumped to large extent either intentionally or accidently to nearby places of electroplating / paint and laundry units at Coimbatore, Tamil Nadu. Thence, the problem conquers alarming proportions in industries percolating Pb(II), Ni(II) and Phosphates ions into the field.

3.6 Categorized Materials - Modification

Chemical treatment/ modification of the materials had been carried out to enhance the porosity /surface area.³ Precisely, chemically treated sorbents exposed better sorption capacity than untreated. The common agents employed for modification/treatment of sorbents are hydrochloric acid, sulphuric acid, phosphoric acid, sodium hydroxide and zinc chloride. Also, it is obvious from literature studies⁴, that sorbents treated with hydrochloric acid⁵ and sodium hydroxide exhibited better surface area due to the conversion of macropores into micropores resulting in better adsorption. In the present work, the categorized materials were treated with hydrochloric acid and sodium hydroxide to enhance maximum sorptive efficiency.

The identified sorbent species were thoroughly washed with doubly distilled water and dried in air. The dried shells were then powdered and sieved to various sizes viz., 85 BSS, 72 BSS, 52 BSS, 36 BSS and 22 BSS. Sieved species were immersed in 0.1 N HCl and boiled for three hours. After decanting the solution, the residues were boiled with 0.1 N NaOH as done before. The treated materials of varying sieve sizes were washed several times well with double distilled water. Later, they were soaked to ensure swelling, as it would make more sorption sites available and finally the sorbent materials were dried in sunlight. The chemically treated *Pistachio vera* shell powder and Bivalve shell powder are denoted as TPVSP and TBVSP in the forthcoming discussions.

3.7 Proximate Analysis: Physico-chemical Characterization Studies

Studies were performed employing modified adsorbents for 0.18 mm particle size.

3.7.1 pH and Conductivity⁶

One gram each of TPVSP and TBVSP were transferred to 250 mL beakers containing 300 mL of previously boiled/ cooled, doubly distilled water. The contents were filtered after 10 minutes, discarding, 15 mL of it in the beginning. The remaining filtrate were subjected to pH and conductivity studies measuring using *ELICO (LI-120)* pH meter and *ELICO (CM 180)* digital conductivity meter respectively, after cooling to room temperature.

3.7.2 Moisture Test : Bidwell- Sterling Method⁶

Moisture contents were determined by Xylene-extraction test method (*ASTM D 2867-95*) and the experimental setup is depicted in figure 3.2

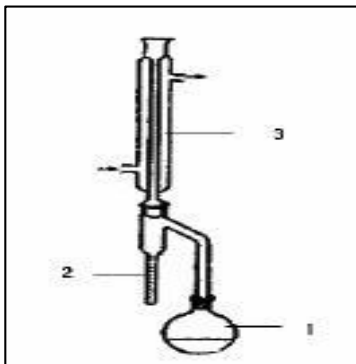


Figure 3.2 Moisture Determination Apparatus

Approximately 0.25g of two adsorbents were taken in two 250 mL Round Bottom flask and 75 mL of Xylene was added, to the set up, followed by injecting Xylene through condensation tube, and filling the water receiving tube. The set up was subjected to heating in such a manner to collect two drops of the distillate per second until all water had apparently been distilled. Moisture content of the samples was calculated as per the equation (1).

$$X = V/m * 100 \quad (1)$$

where,

X - Moisture content of the sample [mL/100 g] (Mass calculation as per the water density of 0.998 at 20⁰C; 20 g/mL).

V - Water volume (Receiving tube) [mL]

m - Sample mass (g).

3.7.3 Bulk Density⁷

Specific gravity bottles of 10 mL capacity were packed with the treated plant and animal shells by thorough tapping with a rubber stopper. The shells¹ mass were weighed, which divided by volume evinced bulk density (g/mL) values.

3.7.4 Specific Gravity⁷

Porcelain dishes with 5g of sorbents and 50 mL of doubly distilled water as contents were boiled gently for 3 min to expel the air. The suspensions were poured into 100 mL pycnometers and weighed (W_c). The same pycnometers were filled with doubly distilled water after W_c measurements and weighed (W_b)

$$\text{Specific Gravity} = \frac{\text{Weight of adsorbent } (W_a)}{\text{Volume of displaced water } (V)} \quad (2)$$

$$V = \frac{W_a + W_b + W_c}{\text{Density of water}}$$

where,

W_a = Weight of adsorbent,

W_b = Weight of pycnometer with water,

W_c = Weight of pycnometer with adsorbent residue

3.7.5 Porosity⁶

The difference between the calculated specific gravity (S) and bulk density (D) values of the samples divided by hundred times the results in porosity value of the samples.

$$\text{Porosity} = \frac{S-D}{S} * 100 \quad (3)$$

3.7.6 Ash Content⁶

Porcelain crucibles with 1 gm of TPVSP and TBVSP were placed in an electric oven maintained at 383 ± 5 K for about 5 h. Later, the contents were ignited in an electric muffle furnace (800 K) for a period of 2 h. The crucibles were cooled in desiccators and then weighed. Heating, cooling and weighing were repeated for every 30 minutes, till the difference between any two consecutive weighing's recorded less than 5 mg. The ash content was calculated as percentage by weight.

3.7.7 Water Soluble Matter⁶

0.5 grams of treated shells along with 60 mL distilled water were boiled with continuous stirring. Later, were allowed to settle and the supernatants were filtered through gooch crucibles, fitted with asbestos mats. The procedure was repeated thrice and the combined filtrates were concentrated to approximately 100 mL, cooled and made up exactly to 100 mL. 50 mL of the concentrates were transferred to china dishes and pre-dried by evaporation on heating in a water bath ensuring, non-spilling of the contents, finally dried in an electric oven (373 ± 5 K), cooled in desiccators and weighed. The procedure of drying and weighing was repeated for every 30 minutes, till the difference between any two consecutive weighing's exhibited less than 5 mg.

$$\text{Water Soluble Matter} = 2000 * W_1 / W_2 (100-X) \quad (4)$$

where,

W_1 = Weight of the residue (g)

W_2 = Weight of the carbon (g)

X = Percentage of moisture in the carbon

3.7.8 Acid Soluble Matter⁶

The treated shells (0.5g) were boiled and stirred with 60 mL of 0.25 N HCl. The same procedure adopted for water soluble matter determination was experimented and the acid soluble matter was calculated as per equation 5.

$$\text{Acid Soluble Matter} = \frac{20000 \times A}{W (100 - X)} \quad (5)$$

where,

A = Weight of the dried residue (g)

W = Weight of the carbon (g)

X = Percentage of moisture in the carbon

3.7.9 Ion Exchange Capacity⁹

0.2 grams of TPVSP and TBVSP were taken in 500 mL beakers and sufficient amount of double distilled water was added for soaking. The slurries were carefully transferred to burettes. The columns were never allowed to drain completely and the levels of the liquids were maintained at a height of about 1 cm above the material bed. 250 mL of the solutions of 0.25 M sodium sulphate was added in drops into the columns at the rate of 2 mL per minute and the samples were collected at the same rate. After column running, the collected samples were titrated against 0.1 N standard NaOH solution using phenolphthalein indicator. The ion exchange capacity of the bed calculated using NV/W , where N is the normality of sodium hydroxide solution; V is its volume and W represents the weight of the treated materials.

3.7.10 Zero point charge (pH_{ZPC})⁸

Zero point charges were determined by the solid addition method, wherein 45 mL KNO_3 solution of 0.1 and 0.01 M concentrations were transferred to 100 mL conical flasks and the pH was adjusted to acidic and basic for 0.1 M to 0.01 M solutions respectively. Later, the total volumes were adjusted to 50 mL by addition of respective solutions. 1 g of TPVSP and TBVSP were added to all flasks, after recording the initial pH of the 50 mL solutions. The suspensions were kept undisturbed for 2 days after vigorous shaking for 5 minutes. The final pH values (pH_f) were recorded. The difference between the two pH recordings ($\Delta\text{pH} = \text{pH}_i - \text{pH}_f$) were plotted against initial pH_i . The zero point charges were arrived from the intersection point of the interpreted plot.

3.7.11 Elemental Analysis

The elementary composition of the chosen materials were determined using CHNS analyser (Elementary Vario EL III-Germany) and the values were expressed in terms of percentage by weight of elemental carbon, hydrogen, nitrogen and sulphur.

3.7.12 Characterization of Surface Functional Groups

Experimental techniques viz., Boehm Method, BET, BJH, FTIR, SEM and EDAX have been employed to reveal the nature of bare, treated and loaded samples along with

the change in their morphologies and concentrations of surface functional groups which could have occurred due to suitable modifications.

3.7.13 Active Sites' Determination

The amounts of oxygenated acid surface groups were determined using Boehm titration method¹⁰. One gram each of the samples were placed in Erlenmeyer flasks, to which 50 mL each of 0.05 N basic solutions (NaOH, Na₂CO₃ and NaHCO₃) were added, shaken for 24 h and the contents were filtered. To 10 mL each of the filtrates 15 mL of 0.05 N HCl was added and the excess HCl was titrated against 0.05 N NaOH using phenolphthalein indicator, followed by Blank experiments. The amounts of acidic sites of various types were calculated on the basis of alkali neutralization of carboxylic, phenolic and lactonic groups which may be present.

3.7.14 Bruner-Emmett-Teller / Barrett-Joyner-Halenda/ FTIR Analyses

Surface area and pore characteristics were determined using Brunauer- Emmet-Teller (BET) and Barrett-Joyner- Halenda (BJH) methods employ nitrogen adsorption on an Accelerated Surface Area and Porosimetry System, (*Micromeritics, BEL, Japan, Inc*), with Belsorp Adsorption/ Desorption analysis software. The procedure included degassing of the samples for 5 hours (120°C) before analysis was followed.

FT-IR analysis were carried out as a pilot and qualitative analysis to determine the main functional groups present in the sorbent that might have involved in the metal uptake. The spectra of the adsorbents before and after metal ion sorption process were recorded using in the range 400 – 4000cm⁻¹.

3.7.15 SEM and EDAX Analyses

Scanning Electron Microscopy (SEM) has been a primary tool for characterizing the surface morphology and the fundamental physical properties of the material surface. It is useful for determining the particle shape, porosity, and appropriate particle size distribution¹¹.The chemical examination of the treated /loaded samples was carried out using an Energy Dispersive X-ray spectrometer (*ZEISS*) attached to a Scanning Electron Microscope (20 kV) under vacuum of 1.33 x 10⁻⁶ m Bar. A thin layer of platinum (10 nm) using a sputter coater was used to cover the materials and later subjected to scan.

3.7.16 Microscopic Analysis

The particle sizes of the chosen materials with different mesh sizes were measured using Nikon Diaphot light Microscope. In order to determine the particle sizes of the adsorbent, the ocular micrometer (10 X dimension) was attached to the microscope was employed. Each division in the scale of the ocular micrometre is 0.01mm. The length and breadth of each granular particle was measured using the ocular micrometre scale. Twelve different particles of each mesh were taken for the average measurement of lengths and breadths, as no two single particles are alike. The sizes were calculated by applying multiplication factors. The particle sizes determined for both the sorbents were against 85 BSS, 72 BSS, 52 BSS, 36 BSS and 22 BSS mesh sizes (0.18 mm, 0.24 mm, 0.30 mm, 0.42 mm & 0.71 mm) respectively

3.8 Preparation of Adsorbate Solutions

Chemicals pertaining to the experimental studies viz., lead nitrate, nickel nitrate, potassium dihydrogen phosphate, ammonium molybdate, sulphuric acid, hydrochloric acid, sodium hydroxide, sodium nitrate, potassium chloride, magnesium sulphate, potassium dichromate, zinc sulphate, buffers pH-4 and pH-9 and were purchased from sigma Aldrich company (Anala R grade) had been employed without any further purifying procedures.

Stock solutions of 1000 mg/L each was prepared by dissolving 1.5985 g of lead nitrate, 4.9546 g of nickel nitrate and 1.4329 g of potassium dihydrogen phosphate using 1000 mL of doubly distilled water (*Distillon 4DQ*). Aliquots of the sorbate solutions of varying concentrations viz., 10 mg/L – 1000mg/L were progressively diluted from the stock solution. pH environments of both the stock and standard aliquots were determined using *ELICO(LI-120)* pH meter after precise standardization with buffers pH 4 and 9.2 respectively.

3.9 Experimental Design

3.9.1 Batch Adsorption Studies

Adsorption experiments were carried out following batch method at ambient temperature, in order to investigate the nature of metal- adsorbent interaction. Influence

of variable operating factors viz., particle sizes (0.18 mm, 0.21 mm, 0.30 mm, 0.42 mm and 0.71 mm), contact time (0, 5, 10, 15, 20, 25, 30 minutes) initial concentrations (10, 25, 50, 75, 100, mg/L) dosages (25, 50, 75 & 100 mg), pH of the medium (3, 5, 7, 9 & 11), influence of cation, anion, co-ions (Na^+ , K^+ , Mg^{2+} , NO_3^- , Cl^- , F^- , SO_4^{2-} , Cr^{6+} , Zn^{2+} , Pb^{2+} and Cu^{2+}) and temperature (293-323 K) were verified under optimized pH to study the sorption characteristics of the employed materials. The determined parameters were considered as the variable, while others were kept constant.

3.10 Analysis of the Samples

A λ_{max} of the initial and residual concentrations of Pb(II) and Ni(II) ions were measured at 324.8nm and 357.9nm, using Atomic Absorption Spectrophotometer: *Shimadzu AA 6200* (Figure 3.3) with high quality acetylene gas were (99.9%) which procured from Covai Air Products, Coimbatore, India. (Duplicate experiments conducted supported the reproducibility of expected values within 2 %) phosphate ion concentrations in the collected samples were analysed at 800nm (λ_{max}) using UV-Visible Spectrophotometer: *Lab India* (Figure 3.4) by Molybdenum blue method, employing Ammonium Molybdate and Stannous Chloride as complexity agents in acidic medium.



Figure 3.3 Atomic Absorption Spectrophotometer (Shimadzu AA 6200)



Figure 3.4 UV- Visible Spectrophotometer (Lab India)

3.11 Data Analysis¹²

The percentage of adsorption of metal ions from aqueous solutions were calculated as

$$\% \text{ Adsorption} = C_i - C_e / C_i * 100 \quad (6)$$

The amount of metal ions sorbed (q) in the sorption systems were calculated according to mass balance equation

$$q_e = V (C_i - C_e) / W \quad (7)$$

where,

V is the volume of the solution (L),

W is the mass of the adsorbent (g),

C_i and C_e are the initial and equilibrium metal concentrations (mg/L) respectively.

3.12 Column Studies

The results of the Batch equilibration method insisted the feasibility and compatibility of the chosen systems based on which the column operations were carried out to quantify the sorbents' efficiencies in a continuous process¹³.

Column experiments were performed using sorbent materials with the fixed particle size (0.18 mm) for the metal ions (initial concentrations: 50-1000 mg/L). Fixed-bed columns, made of cylindrical glass tube (2.5 cm inner diameter and 30 cm

height) were packed with the adsorbent materials between two supporting layers of glass wool, spreaded with the glass beads at the bottom layer of glass wool. The sorbents were loaded from the top of the column and allowed to settle by gravity force.

Metal ions of varying initial concentrations were poured from the top of the column and the flow rate being adjusted by collecting varying volumes of the residual concentrations (metal ion solutions) at pre-set time intervals which depends on the systems' frame work. After performing a series of column studies, based on trial and error method, adsorbent materials suitable for the chosen metal ions exhibiting maximum percentage removal under optimized conditions were fixed on the basis of short term/ long term analyses.

3.13 Desorption

Recycling and recovery of the adsorbents and the metal resource becomes possible by the exploring desorption studies. Sorption of a solute on any adsorbent can either through physical bonding or ion exchange or combination of both. If the adsorption is by physical bonding, then the loosely bound solute can be easily desorbed with distilled water in most cases. Nevertheless, if the mode of adsorption is by ion exchange mechanism, then desorption can be achieved by stronger desorbing agents like acid or alkali solutions.

2 grams of the loaded samples with 100 mg/L metal ion concentrations were taken in 50 mL Erlenmeyer flasks and shaken continuously for 30 minutes, followed by filtration. Later, solid sorbents were gently washed with doubly distilled water. The above procedures were repeated by replacing 50 mL of various strengths of 0.1N HCl and the agitation was continued for 30 minutes before analysis.

The desorption efficiencies¹⁴ were calculated as :

$$\text{Desorption Efficiency} = \text{Amount Desorbed} / \text{Amount Adsorbed} * 100 \quad (8)$$

3.14 Regeneration

Adsorption process is made more economical through necessitating the regeneration of the used-up adsorbents. 100 mg of metal laden sorbents were shaken

continuously with 50 mL HCl as desorbing agent. The desorbed sorbents were washed several times with doubly distilled water until pH of the solution was maintained neutral. aforesaid materials, were dried in an Air oven (378 ± 5 K) followed by sorption experiments. Sorption and desorption cycles were repeated at pre-determined time frames and a change in regeneration was observed through consecutive cycles for three times.

3.15 Collection of Effluent Samples

Effluent samples containing Pb(II) and Ni(II) were collected in pre cleaned PET bottles from electroplating industries at Lakshmi Electroplating Finishers and SIDCO industrial estate (Lead Acid Battery) Coimbatore, India respectively. The initial metal ion concentrations, conductivity and pH of the samples were analyzed using AAS after a series of dilutions.

Effluent samples with 100 mg/L of Pb(II) and 100 mg/L of Ni(II) were subjected to column analysis and the residual concentrations of the eluted samples at a fixed flow rate were analysed.

3.16 Adsorption Isotherm

Adsorption is a solute-solution interface resulting in the migration of particles from the solution to the solute surface, until a dynamic equilibrium is reached amidst the concentrations of the adsorbate in both media. Attainment period of adsorption equilibrium and the specific adsorbate concentration¹⁵ are referred to as equilibrium time and equilibrium concentration, respectively.

The distribution of sorbate species in the liquid phase and its accumulation onto the sorbent is an indicative measure of equilibrium position in the adsorption process thereby, its distribution ratio can be represented by an isotherm. These isotherms describe the interaction pattern of sorbate with sorbents. Quantification of adsorption capacities for chelating Pb(II) and Ni(II) ions using TPVSP and TBVSP were studied employing Langmuir Freundlich and DKR adsorption isotherms.

3.16.1 Langmuir Model

Langmuir isotherm suffices monolayer adsorption onto sorbents' surface with finite number of sorption sites of uniform energy with no transmigration and adsorbate in the surface phase. The Langmuir linear equation¹⁶ is as follows:

$$C_e / q_e = 1/Q b + C_e / Q \quad (9)$$

wherein, adsorption capacity and energy of sorption for the systems are represented as Q and b (Langmuir sorption constant), the equilibrium concentration of adsorbate (mg/L^{-1}) and the amount of metal sorbed per gram of the sorbent at equilibrium (mg/g) are implied as C_e and q_e .

➤ *Equilibrium Factor*¹⁷

The essential characteristics of Langmuir equation are expressed as dimensionless separation parameter ' R_L ' equated to $1/1 + bC_0$, ' b ' being Langmuir constant and ' C_0 ', the initial concentration.

3.16.2 Freundlich Model

Freundlich equation is applicable to heterogeneous surface conditions¹⁸, emphasizing its utility in environmental engineering practice to model the adsorption of pollutants. The linear equation is given as

$$\log q_e = \log k + 1/n \log C_e \quad (10)$$

where, quantity of sorbate ions per unit mass of the sorbent (mg/g) and equilibrium sorbate concentration (mg/L) are represented as q_e and C_e correspondingly.

3.16.4 Dubinin–Kaganer–Radushkevich (DKR) Model

The DKR equation¹⁹ is as follows:

$$\ln C_{\text{ads}} = \ln X_m - \beta \epsilon^2 \quad (11)$$

Where, C_{ads} is the number of metal ions adsorbed per unit weight of adsorbent (mol/g), X_m (mol/g) is the maximum sorption capacity, β ($\text{mol}^2 / \text{J}^2$) is the activity coefficient related to mean sorption energy, and ϵ is the Polanyi potential.

3.17 Activation Factors

Thermodynamic equilibrium constants, K_o for the sorption reaction were determined using Khan and Singh method²⁰. From the plot of K_o against the temperature inverse, the thermodynamic variables, can be calculated as per the equations 12 and 13.

$$\Delta G^\circ = -RT \ln K_o \quad (12)$$

$$\ln K_o = \Delta S^\circ/R - \Delta H^\circ/RT \quad (13)$$

3.18 References

1. Sevcan Ersan, Özlem Üstündağ Güçlü, Reinhold Carle, Ralf Schweiggert, Identification of Phenolic Compounds in Red and Green Pistachio (*Pistacia vera L.*) Hulls (exo- and mesocarp) by HPLC-DAD-ESI-(HR)-MSn, *Journal of Agricultural and Food Chemistry*, 64 (26) (2006) 5334
2. Yang Liu, Changbin Sun, Jin Xu, Youzhi Li, The Use of Raw and Acid-Pretreated Bivalve Mollusk Shells to Remove Metals from Aqueous Solutions, *Journal of Hazardous Materials*, 168 (1) (2009) 156-162.
3. Muhammad Salman, Biosorption of Heavy Metals from Aqueous Solutions using Indigenous and Modified Lingocellulosic Materials, *Reviews in Environmental and Biotechnology*, 14 (2) (2015) 211-228
4. O. F. Olorundare, T. A. M. Msagati, R. W. M. Krause, J. O. Okonkwo and B. B. Mamba, Preparation and Use of Maize Tassels Activated Carbon for the Adsorption of Phenolic Compounds in Environmental Wastewater Samples, *Environmental Science & Pollution Research*, 22 (2015) 5780-5792
5. Isabel Villaescusa, Nuria Fiol, Maria Mortinez, Naria Miralles, Jordi Pochand and Joan Serarols, Removal of Cu(II) and Ni(II) Ions from Aqueous Solution by Grape Stalk Wastes, *Water Research.*, 38 (2004) 992-1002
6. Methods of Sampling and Tests for Activated Carbon used for Decolourising Vegetable Oils and Sugars Solutions, ISI, Indian Standard Institute (1977).
7. S. A. Wilde, G. K. Voigt and J.J. Iyer, Soil and Plant Analysis for Tree Culture, Ed: G. Chesters, 4th edition, Oxford and IBH Publishing Co., New Delhi, India (1972).
8. Tarun Kumar Naiya, Ashim Kumar Bhattacharya, Sailendranath Mandal, Sudip Kumar Das, The Sorption of Lead(II) Ions on Rice Husk Ash, *Journal of Hazardous Materials*, 163 (2009) 1254-1264.
9. D. G. Kinniburgh, J. K. Syeres and M. L. Jackson, Specificadsorption of Trace Amounts of Calcium and Strontium by Hydrous Oxides of Iron and Aluminium, *Soil Science Society of America Proceedings*, 39 (1975) 464-490

10. H. P. Boehm, Some Aspects of the Surface Chemistry of Carbon Blacks and other Carbons, *Carbon*, 32 (1994) 759-769.
11. N.M Andal, N. Shymala Devi and K. Vivithabharathi, Virtual Screening of Treated *Pistachio vera* Shell Powder as a potential sorbent in Sequestering Ubiquitous Divalent Metal Ions from Aqueous Matrices”, *Oriental Journal of Chemistry*, 34(1) (2018) 352-361
12. M. Zabihi, Ali Ahmadpour and A. Haghghi Asl, Removal of Mercury from Water by Carbonaceous Sorbents derived from Walnut Shell, *Journal of Hazardous Materials*, 167 (2009) 230-236,
13. S. Sugashini, K. M. Meera and Sheriffa Begum, Column Adsorption Studies for the Removal of Cr(VI) Ions by Ethylamine Modified Chitosan Carbonized Rice Husk Composite Beads with Modelling and Optimization, *Journal of Chemistry*, 2013 (2012) 1-11
14. S. H. Hasan, K. K. Singh, O. Prakash, M. Talat and Y. S. Ho, Removal of Cr(VI) from Aqueous Solutions using Agricultural Waste Maize Bran, *Journal of Hazardous Materials*, 152 (2008) 356-365.
15. Ahmet Sari, Mustafa Tuzen, Biosorption of Pb(II) and Cd(II) from Aqueous Solution using Green Alga (*Ulvalactuca*) Biomass, *Journal of Hazardous Materials*, 152 (2008) 302- 308.
16. Silke Schiewer, Ankit Balaria, Biosorption of Pb²⁺ by Original and Protonated Citrus Peels: Equilibrium, Kinetics and Mechanisms, *Chemical Engineering Journal*, 146 (2009) 211-219.
17. Zouhair Elouear, J Bouzid, N Boujelben, Removal of Nickel and Cadmium from Aqueous Solutions by Sewage Sludge Ash: Study in Single and Binary Systems, *Journal of Environmental Technology*, 30 (6) (2009) 561-570
18. Hanim Awab, *Thanalechumi Paramalingam* Mussel Shell and Waterworks Sludge as Sorbent Materials for the Removal of Cu(II) from Aqueous Solution, *Journal of Fundamental Science*, 7 (2) (2003) 113-119

19. Ozgur Dogan Uluozlu, Ahmet Sari, Mustafa Tuzen, Mustafa Soylak, Bio Sorption of Pb(II) and Cr(III) from Aqueous Solution by Lichen (*Parmelinatiliaceae*) biomass, *Bioresource Technology*, 99 (2008) 2972-2980.
20. A.A.Khan and R.P.Singh, *Colloid Surface*, 24,33(1987)