

**Synthesis and characterization of Na<sub>2</sub>SeO<sub>3</sub>/orange peel  
Nanocomposite and its evaluation as an effective adsorbent for the  
removal of heavy metals from wastewater**



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**(2021)**

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

## **The Exordium**

**“In the name of Allah the compassionate the merciful”**

All the accumulation and admiration is for Almighty Allah the most merciful, gracious and beneficent who is entire source of all the Knowledge and wisdom endowed to mankind. I offer my humble thank from the core of my heart to Holy prophet Muhammad (S.A.W.W), who is forever source of guidance and knowledge for the humanity.

**“Praise to Allah, the Lord of creation, the Compassionate, the Merciful, the King of the Judgment day! Alone”.**

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Date: -----

**Final Approval**

It is certified that we have read the thesis “**Synthesis and characterization of  $\text{Na}_2\text{SeO}_3$ /orange peel Nanocomposite and its evaluation as an effective adsorbent for the removal of heavy metals from wastewater**” submitted by Ms. Maria Aziz and it is our judgment that this project is of sufficient standard to warrant its acceptance by the International Islamic University Islamabad for the MS degree in Environmental Science.

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*A thesis submitted to Department of Environmental Science, International  
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award of the degree of MS Environmental Science*

## DECLARATION

I hereby declare that the work presented in this report is my own effort except where otherwise acknowledged and that the report is my own composition. No part of this project report has been previously presented for any other degree.

Date: -----

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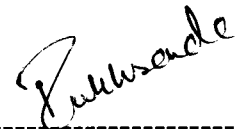
Maria Aziz

## DEDICATION

I dedicate this thesis to my Supervisor *Dr.Rukhsanda Aziz* who has offered me unwavering support, guidance, help and encouragement during my MS journey. Moreover I dedicate my thesis to my *Parents* and *Siblings* as their never ending support, encouragement, patience and assistance has helped me to achieve this goal.

## Forwarding sheet

This thesis entitled “Synthesis and characterization of  $\text{Na}_2\text{SeO}_3$ /orange peel Nanocomposite and its evaluation as an effective adsorbent for the removal of heavy metals from wastewater” submitted by Ms. Maria Aziz in partial fulfillment of MS Environmental Science has been completed under my supervision and guidance. I am satisfied with the quality of student’s research work and allow her to submit for further process as per IIUI rules and regulations.



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Dr. Rukhsanda Aziz

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## List of Abbreviations

|                                 |   |
|---------------------------------|---|
| Pb                              | Lead                                    |
| Cr                              | Chromium                                |
| Se                              | Selenium                                |
| AC                              | Activated Carbon                        |
| NC                              | Nanocomposite                           |
| OP                              | Orange Peels                            |
| AOP                             | Activated Orange Peels                  |
| NAOP                            | Non-activated Orange Peels              |
| Rpm                             | Rotation per minute                     |
| MCLs                            | Maximum contamination levels            |
| Se/OP                           | Selenium/Orange peel nanocomposite      |
| K <sub>2</sub> CrO <sub>4</sub> | Potassium Chromate                      |
| HCl                             | Hydrochloric Acid                       |
| NaOH                            | Sodium Hydroxide                        |
| NP                              | Nanoparticles                           |
| FT-IR                           | Fourier Transform Infrared Spectroscopy |
| SEM                             | Scanning Electron Microscopy            |
| XRD                             | X-Ray Diffraction                       |
| AAS                             | Atomic Adsorption Spectrophotometer     |

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## Abstract

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### Abstract

Heavy metals are the most dangerous types of contaminants among all the pollutants found in water and are of major concern because they are non-biodegradable in nature, highly toxic even at very low concentrations and have serious effects on both human and environmental health. So this research study aimed to assess the efficiency of commercially available orange peel waste (low cost adsorbent) for the treatment of synthetic wastewater containing heavy metals as an economical water cleaning technology. Therefore orange peel adsorbent was doped with selenium nanoparticles to enhance the adsorption capacity. Batch experiments were conducted with two different heavy metals i.e. Pb and Cr to investigate and examine the effect of initial concentration, adsorbent dose, and temperature, effect of pH, and contact time on the adsorption of selected heavy metals.

The adsorption characteristics of material were determined through its physical and chemical properties (surface area and functional groups). The present study reported that orange peel nano-composite acts as a good adsorbent and suitable alternative water cleaning technology for removing heavy metals.

The adsorbent characterization was performed through SEM, FT-IR and XRD, while Atomic Adsorption Spectroscopy analysis was performed to obtain the heavy metal concentration after contact between adsorbate (Pb and Cr) and adsorbent (Se/OP Nano-composite). According to the results it is depicted that Se/OP Nano-composite works very effectively under optimum conditions for removing selected metals (Pb and Cr). Large amounts of Pb and Cr were removed at basic pH with 20ppm heavy metal concentration which is 99.9% and 99.99% at 10mg dose. So 10mg is considered as the optimum dose for the removal of both Pb and Cr.

It is concluded that activated carbon prepared from orange peels can be a low cost bio-adsorbent (alternative cleaning technology) for the treatment of wastewater containing heavy metals, as it is abundantly available in agricultural countries.

# **CHAPTER #1**

## **INTRODUCTION**

## 1.0. Introduction

Fresh water is considered as for 3% of total water resources present on the Earth. Waste effluents containing heavy metals get discharge directly into the water resources causing serious threats to both human and ecosystem through different human and industrial activities. Fresh water bodies are the sources from where the water fit for human consumption is obtained. About 70% clean water goes to agriculture and this natural resource is now becoming insufficient so its scarcity is a major social as well as economic concern (Baroni L et al., 2007). Over a larger scale, industrialization cause environmental pollution specifically water pollution where lakes and rivers are overburden with large number of toxic materials and effluents (Vieira RH, Volesky B., 2000).

They are introduced naturally (weathering of the parent materials) as well as through anthropogenic activities which includes mining, electroplating, smelting, and different other industrial processes (Alloway., 1995 and Nriagu, 1996). This situation affects consequently ground and surface water. Hence it is crucial to remove these hazardous organic pollutants from waste water (Khan et al., 2012). Heavy metals are highly toxic elements and have non thermo-degradable and non-biodegradable nature(Bohn et al., 1985).They are considered as a major threat to environmental pollution throughout the world (Ping et al., 2011).

There are extensive issues of pollution caused by heavy metals as they are harmful and hazardous for animals and plants as well as human beings (Jang et al., 2006; Li et al., 2006 and Zhuang et al., 2009). So presence of toxic contaminants (heavy metals) in water creates serious health and environmental hazards.

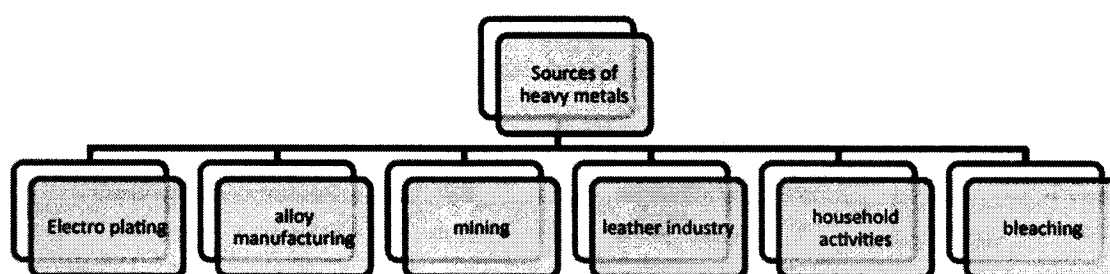


Figure 1: Main sources of heavy metals.

There are number of health problems that can be caused by polluted water with metals (Igwe and Abia, 2007) stated that Lead can inhibit enzyme activities and formation of red blood cells; it can effect nervous system as well even at low concentration. Manganese and Cadmium can affect growth and skeletal calcification and also have long term effect. Because of technical and economical limitations several countries release their effluent without any treatment to surface water (Michael et al., 2003).

| Threats       | Estimated population at risk (million people) | Estimated global impact (million people) |
|---------------|---|--|
| Lead          | 10  | 18-22                                    |
| Mercury       | 8.6   | 15-19                                    |
| Chromium      | 7.3   | 13-17                                    |
| Arsenic       | 3.7   | 5-9                                      |
| Pesticides    | 3.4   | 5-8                                      |
| Radionuclides | 3.3   | 5-8                                      |

**Table 1: Top six toxic threats.**

Wastewater treatment plants are in the matter of in connection with cost and these plants also have many other problems related to disposal (Mansour HF, 2013). To conquer this problem different fruit wastes are used as an efficient bio-adsorbent for treatment and management of wastewater. The technique which is the most efficient and economical as well as it does not require the use of energy for cleaning of wastewater is adsorption; this technology is ecofriendly (Palanisamy P et al., 2013).

| Removal techniques  | Advantages   | Disadvantages  | Cost              | References             |
|---------------------|--|--|-------------------|------------------------|
| Precipitation       | Simple and low cost  | Slow process and produce large sludge                    | Lower             | Choong et al., 2007    |
| Electrodialysis     | High separation selectivity                                    | High energy consumption                                  | High              | Mohammadi et al., 2005 |
| Membrane filtration | No chemicals required, taste and color is not affected by dose | Temperature limitation, effective for minor stream sizes | High              | Hosamani et al., 2010  |
| Coagulation         | Simple chemicals used  | Produce toxic sludge                                     | Comparatively low | Zhang et al., 2011     |

**Table 2: Advantages and disadvantages of conventional technologies used for the removal of heavy metals from waste water.**

Treatment technologies for both drinking water and wastewater are one of the most important key requirements for sustaining human well-being as well as for rising the economy.

So, it is pivotal to introduce, then accomplish advanced and unconventional water treatment technologies at very low energy consumption as well as higher efficiencies (Zwiener, C et al., 2007). The outdated materials and cleaning technologies including oxidation, nanofiltration (NF), activated sludge (AS), activated carbon (AC) and reverse osmosis (RO) are insufficient and ineffective to clean polluted waters particularly which contain surfactants, pharmaceuticals, personal care products, and different industrial extracts. The traditional waste water treatment technologies have insufficient potential for acceptable elimination of pathogenic microorganisms and a widespread range of hazardous substances and pollutants in wastewater. Problems of energy shortages, water shortages, health, and climate change can be reduced using better purification technologies.

There is a need to develop profitable, economical, efficient and authentic materials and technologies to accomplish a significant saving of clean water by reusing of wastewater (J. W. Readman et al., 2002).

Previous works showed appropriateness of variety of agricultural provisions (materials) including corncob, coconut coir pith (Shankar, 2014), rice husk (Sivakumar, 2014 Sivakumar and Nouri, 2015), groundnut husk, tamarind kernel (Shanthi and Mahalakshmi, 2012; Sivakumar, 2014), saw dust, tea leaves carbon, and different other bio-materials that can be used to treat wastewater (Sivakumar, 2012).

Various fruit wastes and agro wastes are utilized as adsorbents for the treatment of wastewater, like orange peel (Adeleke H et al., 2018), banana peel (Nguyen T et al., 2012), pomegranate (Jaouali I et al., 2018), Corn Cob (Panphrom S et al., 2012) and agricultural wastes (Sultan M et al., 2018). 20% population of Pakistan is approachable to safe drinking water which is disgusting and shocking situation for the upcoming generation in future. Therefore it is necessary to treat the wastewater through technologies that must be cost effective, efficient, as well as economical for removing the contaminants from wastewater (K.M. Al-Qahtani 2016).

Elimination of hazardous materials from contaminated water is essential for both human health and ecosystem defense. So in this perspective, different conventional technologies including adsorption, precipitation, oxidation, reduction, and ion exchange are used usually. Among them the process of adsorption is the most appropriate technology due to its high competence as well as profitable consideration (Gupta, V et al., 2016). Numerous marketable and traditional technologies are proceeding daily but the development of nanotechnology has evidenced as one of the most advanced and innovative way for the treatment of wastewater. Advances in nano scale investigation and research made it evident and promising to develop stable economical and environment friendly treatment methods and technologies for the treatment of wastewater efficiently in order to meet the standards of water quality that are ever increasing. Nanotechnological developments and improvements are providing the chances and to encounter the stresses of drinking water for future generations. So it is recommended that by using variety of nanoparticles under the subject of nanotechnology it is possible to address different water related concerns sufficiently (N. Savage and M. S. Diallo 2003).

Adsorbents such as zeolites, activated carbon, polymers, and biomaterials are using on large scale for the treatment of wastewater (Gupta, et al., 2015). Still, the removal efficiency of these resources is comparatively less (Gupta, Vet al., 2016). Consequently, it has become vital to find more competent and capable adsorbents.

Since the developments in nanotechnology became advanced, there is a great potential for the treatment and remediation of environmental problems (Gupta, et al., 2015). In contrast to traditional materials, the adsorbents doped with nano-particles show greater adsorption rates and higher competence for the treatment of wastewater, may be due to the extremely large surface area (Dil, et al., 2017). Different cost effective, resourceful, and environment friendly nanomaterial have been proposed for decontamination of wastewater because of having unique properties and functions (Sadegh, et al., 2016).

The perfect adsorbent for treatment of wastewater should fulfil the following criteria (Gupta, et al., 2016).

- Environment friendly and nonthreatening
- Determine a high adsorption capacity and great discrimination particularly for the contaminants at very low concentration.
- Must be eco-friendly

Newly, research for decontamination of industrial waste by removing toxic metals has motivated the use of agricultural by-products as an adsorbents through the process of adsorption. As the agricultural wastes are available in sufficient quantities in agricultural countries it make possible to use them as a natural adsorbents. Agronomic materials include a variety of functional groups, lignin, lipids proteins, hydrocarbons and starch. Recent advances and developments in nanotechnology provides great opportunities to find profitable as well as maintainable water stock systems. The diverse functional capabilities associated with nano-science is expected to offer reasonable, great performance solutions for the treatment of wastewater which require less infrastructure (Qu et al.2013).

Wastewater treatment technologies related to nano-technology are encouraging to overcome the challenges regarding wastewater treatment. These technologies offer advanced treatment capabilities as well (Bunani et al. 2015). The worth and value of the waste can be enhanced affectedly through nano-technology which comprise microfiltration, nano-filtration and reverse osmosis. It also enlighten the economic and environmental development of organizations to produce and improve better quality water for future generations (Wu et al. 2011). The management and recycling of wastewater can be achieved through using nanotechnology which provide greater chances to eliminate distresses associated with water.

It require less dependence on large infrastructure. Nanotechnological water treatment technologies are achieving much focus and concentration in developing countries (urban areas) that mark an extensive variety of contaminants. A viable municipal water management is a definitive and ultimate aim which can be reached by implementing supreme management systems with engineered nanomaterials (He et al., 2010). Adsorbents are nano scale small particles having abundant fascination to adsorb pollutants from aqueous solutions (Madhura et al. 2018).

These adsorbents may be used effectively as well-organized, economical and eco-friendly adsorbents in order to remove several toxic substances from aqueous solutions like azo dyes and heavy metals (Singh, S et al., 2011). The process of adsorption is a spectacle in which the adsorbate is added on the adsorbent surface where a solution having absorbable solute approaches to contact with a solid with a extremely porous surface, then due to liquid–solid intermolecular forces of attraction some of the solute molecules are deposited on the solid surface (Wang, L et al., 2012). Application of nanoparticles can be linked with many fields like medical, environmental studies, energy generation, food industries, electronics production, and agriculture (Wang, Y. and Herron, N., 1991).

The most frequently used nanoparticles which have widespread uses are silver, zinc, gold, copper, iron and selenium. Essential mineral selenium is a metalloid and an essential micronutrient. It plays vital roles in the human body by improving the action of enzymes like seleno-enzymes and glutathione peroxidase that protect the body in contradiction of immunity related diseases (Romero-Perez, A et al., 2010).

Nanoparticles uses in communal customer products and machines because of their unique properties than bulk materials (Crutzen, et al., 2014). Selenium is an important trace element in the diet, required for maintenance of health and growth (Skalickova, et al., 2017).

The waste of orange peels is generated mostly from juice manufacturing industries which cause different health environment (soil and water pollution) related problems because of production of bulk amounts. soil and water pollution. Therefore, reclamation and conversion of orange peel waste has been a hot topic of concentration recently and it is one of the most important alternatives for the preparation of sorbent materials. Orange peels as a sorbent can be used to eradicate contaminants such as color and chemical oxygen demand from wastewater. Orange peels are produced in large amounts throughout the Pakistan mostly from juicing industries so it can be used as an economical bio-sorbent for the treatment of pollutants present in aqueous media.

This present study deals with the assessment of efficiency and effectiveness of selenium nanocomposite with orange peel for treatment of synthesized wastewater and the probability of removing selected heavy metals from water polluted with Pb and Cr. So this study will provide a reference document for adsorption capacity of Se/orange peel nano-composite by using nanotechnology.

### **1.1. Problem Statement**

As a result of different anthropogenic activities, today world is facing serious threats of air, water and land pollutions particularly pollution of water, has raised up severe environmental influences. Production of large volumes of contaminated water polluted with different heavy metals has put a lot of stress on the human beings and environment. Different treatment technologies are available to control water pollution but the drawback of operational & maintenance cost and complicated procedure involved in the treatment is associated with them.

## **1.2. Aim of the study**

The aim of the present study is to examine the removal efficiency of Se/orange peel nanocomposite as a low cost bio-adsorbent for the removal of selected heavy metals (Pb and Cr) from synthetic wastewater.

## **1.3. Objectives**

Therefore objectives of my study:

- 1) To synthesize and characterize the dried orange peel nano-composites.
- 2) To investigate the removal efficiency of orange peels as an adsorbent to minimize the treatment cost.
- 3) To study the effect of pH, initial metal ion concentration, dose and time required for bio-sorption

## **CHAPTER #2**

# **LITERATURE REVIEW**

## 2.0. Literature review

Water is an important component for living organisms and its pollution is one of the major worldwide environmental threats today. Invasion of substantial quantities of surfactants, organic and inorganic waste, sediments, sewage, synthetic dyes, and heavy metals into all types of water bodies has been increasing at faster rate over the past century because of rapid industrialization, population growth, agricultural activities and other environmental and geological changes. Fresh water that is free of contaminants and poisonous substances, is vigorous to the biosphere's health, as well as serious feedstock in different industries. Significant consideration has been rewarded to the environmental complications and harms concerning treatment of water recently (N. Savage, M. S and Diallo, J. 2005).

Predominantly, the dyes are matter of great concern present in industrial wastewaters because they have toxic and potentially dangerous moieties as well as being the source of aesthetic problems (Javed, M and Usmani, N., 2013). The problems existing by such wastes are the hot and critical issue for the most of developing countries including Pakistan. These pollutants are very damaging and are threatening seriously. Therefore there is a dire need to develop such technologies that are environment friendly and economical to remove pollutants. At present there are a number of methods that are in operation to remove and minimize these wastes are including ion exchange, electro-coagulation, membrane filtration, advanced oxidation, biological degradation, photo catalytic degradation and adsorption.

20% population of Pakistan have access to nontoxic drinking water which is a frightening condition for the upcoming generations in future. So it is obvious to clean wastewater through such technologies that must be cost effective, inexpensive, ecofriendly, effective as well as competent for the elimination of contaminants from wastewater (K.M. Al-Qahtani 2016). Various natural biosorbents are present in environment having the capability to treat water contaminated with heavy metals. A variety of used materials such as rice husk, fruit waste, peat moss, red mud, zeolites, fly ash and sugar industry waste have removed numerous organic pollutants from 80-99.9% (Khan et al., 2012; Gangadhar et al., 2016 and Nuruzzaman et al., 2016).

Bio-sorption is recognized as one of the greatest technologies for cleansing and refining of water due to its economical, cost effective and environment friendly properties. This process is resilient enough to appreciate the requirement of water reuse and extraordinary overspill standards in the industries. Bio-sorption is principally a mass transmission process through which the metal ions are transferred from the solution to the sorbent and then bound by physical or chemical associations (Agarwal et al., 2011, Gupta, et al., 1998, Gupta and Nayak, 2012, Babel, and Kurniawan, 2005). Dissolved pollutants (organic and inorganic) of water can be eliminated through an effective adsorption technique (Gwenzi et al., 2017).

### 2.1. Agricultural waste

Agricultural wastes can also be used as sorbents to remove contaminants (heavy metals) from aqueous solutions. Because of plentiful accessibility of agricultural by products like rice husk which is economical as well as serious disposal problem is associated with it, agricultural waste can be considered as one of the richest source for low cost adsorbents (Selvakumari et al., 2002). In previous literature Ni in wastewater was treated with orange peel (Ajmal et al., 2000). Numerous low cost bioadsorbents have been recognized including orange peel, sawdust, cellulose waste, sunflower waste and palm-fruits etc. and these are cost effective as well as accessible over a large scale.

Recent consideration has been rewarded for manufacturing nano-bioadsorbents to increase the removal efficiency and large accessibility of adsorbent i.e. cost effective agricultural waste is altered into nano-scale adsorbents by several physical or chemical processes. Studies showed that most of the wheat straw has been left for burning directly so it is essential to make its best use to avoid pollution. Therefore Huang et al., have conducted a research study on structure, morphology and components of wheat straw which has a vascular bundle arrangement and offer extra surface area for the alteration of chemicals (Huang et al., 2005).

Activated rice husk waste is potentially a beneficial material for the elimination of Cu and Pb from aqueous media (Wong et al., 2003). Orange peel is one of the low cost adsorbents used to treat wastewater. Agrarian wastes particularly, waste having high percentage of lignin and cellulose comprises polar functional groups including amino, carbonyl, alcoholic, phenolic and ether groups which have great capacity for metal binding (Hossain M et al., 2012).

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**Synthesis and characterization of Na<sub>2</sub>SeO<sub>3</sub>/orange peel Nanocomposite and its evaluation as an effective adsorbent for the removal of Heavy Metals from wastewater**

| Agricultural waste | Metal they removed                     | References  |
|--------------------|--|---|
| Tea industry waste | Cd (II), Cu (II)<br>Ni (II)<br>Cr (VI) | Ozasik et al., 2004<br>Maloc and Nuhoglu, 2017<br>Maloc and Nuhoglu, 2017 |
| Potato peels       | Cu (II)                                | Amana et al., 2017  |
| Cork powder        | Zn (II)                                | Kanawade and Gaikwad, 2011  |
| Water melon shell  | Cu (II)                                | Banerjee et al., 2004   |
| Grape stalk wastes | Cu (II), Ni (II)                       | Villaescusa et al., 2004  |

**Table 3: Removal of heavy metals by agricultural waste from waste water**

## 2.2. Activated carbon

Activated carbon (AC) is one of the most extensively used adsorbents which is extremely porous, shapeless solid comprising of micro crystallites with a graphite lattice, commonly produced in small pellets or in a powder form. Most commonly used adsorbents for the removal of metal ions are biomaterials, zeolites and industrial solid wastes (Wang et al, 2008), clay minerals (Wilson et al. 2006) and activated carbon (Satapathy et al., 2006, Pollard et al., 1992).

Contemporary and advanced industries started manufacturing of activated carbon in 1900–1901 in order to substitute bone char in the sugar purifying industry (Bansal et al., 1988) and ground (powdered) activated carbon was produced first time commercially in Europe in the initial era of 19th century, through spending wood as a raw material (Mantell et al., 1968). It can be produced from any material ensuring high content of carbon. As it has advanced permeable structure and large surface area for adsorption of heavy metals so it is a good adsorbent for the elimination of chromium (Anirudhan and Sreekumari, 2011).

For the very first time activated carbon was used as an adsorbent for the treatment of waste water in 1940, but it cannot be used in large amount concerning high cost. So this situation compelled scientists in the direction of the development of low cost options of activated carbon (Khan et al., 2012).

Activated carbon is synthesized from vineyard shoot where phosphoric acid was used as an activating agent whose permeability was better when the raw material was activated (Corcho et al., 2006). Large surface area and enormous pore size makes activated carbon as a best adsorbent for the treatment of contaminated water to remove of heavy metals (Fabregat et al., 2012). These materials are nearby accessible in huge quantities so, they are economical (Mohana et al., 2007). Activated carbon (AC) is now produced from different agro-based wastes which include moso and bamboo (Lo et al., 2012), hazelnut shell activated carbon (Koby 2004), rubber wood sawdust (Karthikeyan et al., 2005), treated sawdust of Indian rose wood (Garg et al., 2004) coconut shell carbon (Babel & Kurniawan 2004), coconut tree sawdust (Selvi et al., 2001), sugarcane bagasse (Sharma & Forster 1994), viticulture industry wastes, lex, grape stalk, pomace (Sardella et al., 2015), and wood activated carbon (Selomulya et al., 1999).

Chromium was removed from wastewater through the use of activated carbon produced from rubber wood sawdust from which the adsorption capacity of maximum 44 mg/g was achieved at optimum of pH 2 (Karthikeyan et al., 2005). Because of containing pectin (galacturonic acid), cellulose, lignin and hemicelluloses, orange peel waste is recycled and used as a bio-adsorbent for the elimination of chromium from wastewater. Because of its easy accessibility and low cost it is very attractive adsorbent (Feng et al., 2011).

### **2.3. Nanotechnology**

The advances in nano-science recommends the nanotechnology as beneficial technology for resolving most of the current water treatment issues by using nano-sorbents, catalytic membranes, bioactive nanoparticles, nano-catalysts etc. (Diallo, J, M. S and N. Savage, 2005). Nanotechnology is low-cost technique that does not include sophisticated equipment and long procedure. The process is simple, easy, and safe to handle, and work effectively (Khatamian, M et al., 2017). At present, numerous nano-substances are manufactured with the help of this deriving technology which has great significance in scientific research (Maynard, A. D et al., 2004). Nano-composites and nano-sized metal oxides cleanup water under the several water quality limitations such as competing ions and pH (Sunbaek, B et al., 2010).

Nanoparticles are a new cohort of such materials that are highlighted for the remediation and treatment of environment because of having unique possessions like magnetic property, small particle size, big surface area, pore size, biocompatibility, thermal strength, and chemical inertness (Ahmed et al., 2015).

High surface area, high active sites, low particle diameter and magnetic character of adsorbent are accountable for the higher removal capability for pollutants (Herrero, R et al., 2016). Recently, nano-composites, metal-based adsorbents and metal oxides are applied for cleanup of pollutants from pollutant sites (Hmidi, N et al., 2017). Moreover, development and redevelopment of adsorbent make the process important in respect to cost and removal capacity (Musmarra, D et al., 2009). Adsorption is extra trustworthy, encouraging process having competence, working simplicity, cost effectiveness, local accessibility of adsorbents and regeneration potential of the adsorbents (Musico et al., 2013, Kumar et al., 2014, Joshi et al., 2018 and Thitame and Shukla, 2017).

Various cost effective, efficient and environment friendly nano-materials having distinctive functional properties are suggested for possible uses in cleansing of groundwater, drinking water, industrial effluents and surface water (Savage, N., and Diallo, M.S, 2005, Theron, J et al., 2008, Sadegh, H et al., 2016, Asfaram, A. et al., 2017). It was revealed that the nano-materials may play a significant part in the treatment of waste water (Singh, S., 2013). The nano-materials may be effectively used as operative, economical and environment pleasant adsorbents to eliminate several contaminated substances from wastewater like heavy metals and azo dyes etc. (Zwiener, C et al., 2007, Joss, A et al., 2006, Sadegh, H et al., 2016, Savage, N., and Diallo, M.S, 2005, Singh, S., et al., 2011, Tuzen, M., and Soylak, M 2007, Zhao, Y.-G et al., 2010).

Nanotechnological developments are providing the chances to encounter the demands of fresh water for future generations. Now it is recommended that it can sufficiently report most of the water quality related concerns and problems through using variety of nanoparticles (N. Savage and M. S. Diallo 2003). Currently, nano-materials are providing promising methodology for the removal of heavy metals from wastewater.

Over the previous limited years, nano-materials have drawn-out a lot of attention. The earlier time spans countersigned the growing uses of nano-materials in the environmental safety field as well (Kharisov, B.I. et al., 2014). Remarkable research on nano-materials have been accepted out to examine their uses in water treatment for the removal of heavy metals and they have proved great potential as a promising and positive substitute to remove heavy metals from wastewater (Vunain, E et al., 2016, Nizamuddin, S et al., 2018).

Carbon-based nano-materials were primarily used in the electronics industry due to their astonishing electrical and thermal properties (Dresselhaus, M.S and Terrones, M. 2013). However, some other extraordinary properties they exhibited are; simplicity of chemical or physical modification, capability of removing both organic, and inorganic pollutants large surface area, have prepared carbon-based nano-materials as ultimate substitutes for handling wastewater (Rodrigues, D.F 2015).

Wastewater treatment plants concerning cost contribution and these plants have also problems related to dumping (AG E-S, and Mansour HF 2013). To overwhelm this problem fruit waste is used as cost effective and economical adsorbent for treatment of wastewater. Adsorption is a technique that is most efficient, profitable and cost effective as well as it does not require the use of energy for the treatment of contaminated water; this technology is eco-friendly (Baseri JR et al., 2012). Various agricultural wastes and fruit waste are used as adsorbents for the treatment of water, such as banana peel (M. Hossain et al., 2012 and R. Olaoye et al., 2018), orange peel (A. Pandiarajan et al., 2018), pomegranate (Jaouali I et al., 2017), and agricultural wastes (Sultan M, et al., 2018, Hassoon HA (2018) and Ibrahim S, *et al.*, 2004).

Wannahari M ,et al., 2018 used nano-magnetic adsorbent composite produced from sugarcane bagasse for removing copper from contaminated water, adsorption-desorption studies indicated that it can demonstrate high stability for regeneration with good re-adoptability (Kumari et al., 2018). Tellez k, et al., 2011 adsorbed chromium through a composite by incorporating nanoparticles of iron into orange peel pith and it was investigated the % removal and adsorption capacity for this composite were 71% and 5.37 mg/g correspondingly than raw orange peel that was 34% and 1.90 mg/g respectively.

To control water pollution number of treatment technologies are available but the drawback of higher operational cost, complicated procedures involved and the generation of toxic sludge is associated with them. So the scope of this contemporary research is to examine the adsorption capacity of orange peels applied as an adsorbent for the treatment of contaminated water containing selected heavy metals. As the waste produced from fruits is discarded and dumped openly in our country which may cause different environmental problems including leachate that will ultimately damage and destroy earth. Therefore this contemporary research study on wastewater treatment will provide the idea for treating contaminated water through using orange peels waste as an efficient and economical adsorbent.

# **CHAPTER #3**

## **METHODOLOGY**

### **3.0. Material and Methods**

#### **3.1. Sampling**

The samples of Orange peels were collected from local market of Islamabad as its availability, handling and transportation is stress free and very easy.

#### **3.2. Adsorbent**

Selenium/Orange peel nanocomposite

##### **3.3.0. Preparation of Adsorbent**

Orange peels samples were collected from local market of Islamabad, cut down into pieces, and washed two to three times by using tap water to remove extraneous materials (dirt and sands). After washing these sample materials were dried in the presence of sunlight for one week. Then dried orange peel samples were crushed to a powder form with the help of grinder. After that samples (crushed powder) were washed again by using de-ionized water till it became colorless. Then finally it was dried at 60°C for seven hours in drying oven.

##### **3.3.1. Activation of the Adsorbent**

For the activation of adsorbent 10g of properly dried orange peel and 100ml 2M NaOH solutions were prepared and placed in 500ml reaction kettle then heated at 200rpm at 100°C for 7 hours. After that resulted orange peel sample was sieved and washed through using de-ionized water till the filtrate became colorless and neutral. Approximately after two to three days of continuous washing it became colorless and neutral, then it was treated with Hydrochloric acid (2M) under water bath at 80°C for 25-30 minutes to remove residual alkali metals in samples. At the end this prepared activated orange peel sample was washed by using de-ionized water till it became colorless and neutral. Then finally it was dried in drying oven at 80°C for 4 hours (Kaifeng et al., 2019).

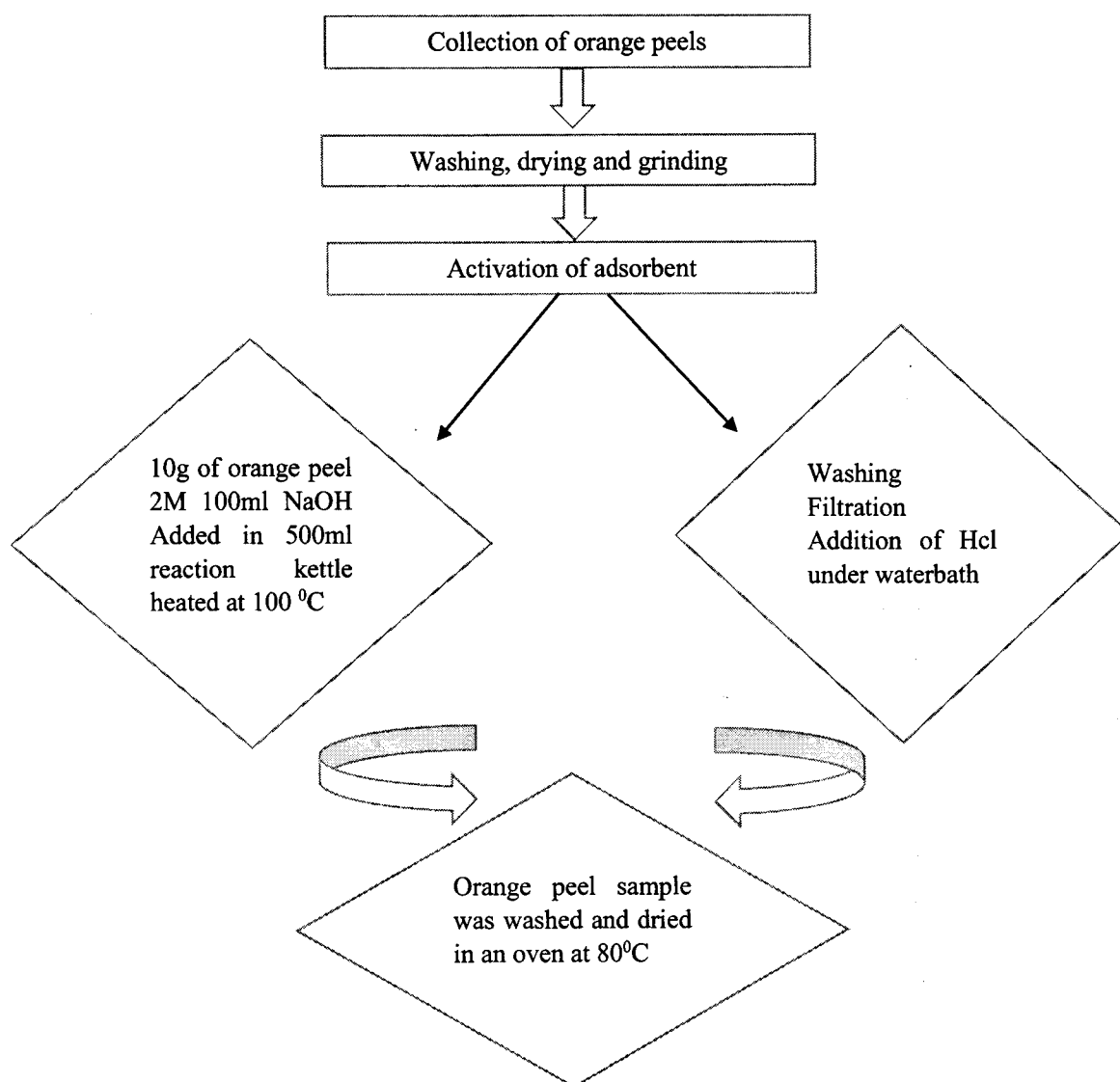


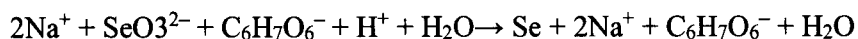
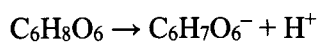
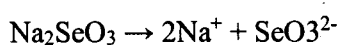
Figure 2: Flow sheet diagram of activation of Orange Peel

### 3.3.2. Synthesis of Selenium Nanoparticles

Selenium nanoparticles (SENPs) were prepared by chemical precipitation/reduction method. Sodium selenite ( $\text{Na}_2\text{SeO}_3$ ) and ascorbic acid ( $\text{C}_6\text{H}_8\text{O}_6$ ) were used for the preparation of nanoparticles of Se where ascorbic acid ( $\text{C}_6\text{H}_8\text{O}_6$ ) act as a reducing operator (Malhotra Set al., 2014).

Then aqueous solution of 17.29g Na<sub>2</sub>SeO<sub>3</sub> and 8.806g C<sub>6</sub>H<sub>8</sub>O<sub>6</sub> were prepared in ratio of 1: 4. After that solution was kept under magnetic stirring condition at different rpm (rotation per minute) and at ambient temperature for 30 min.

Then the mixtures were allowed to react with each other in the concentrated form until the color of solution change from colorless to red color. Finally when red color appeared then the solution was centrifuged at 3000 rpm (rotation per minute) and the selenium nanoparticles were obtained and placed in a desiccator to dry at room temperature.



### 3.3.3 Preparation of nanocomposite of Se and orange peel-Cellulose (OPC)

3g of orange peel cellulose was mixed with 7g of Se nanoparticles, then mixture was added in 30 mL of distilled water and agitated for half an hour with the help of magnetic stirrer. After that it was shifted to a 50 mL vessel and heated on hot plate with magnetic stirring at 200°C for 24 h, then resulted sample was washed two times using both ethanol and distilled water. After that it was dried at 60 °C in drying oven and named as Se/Orange peel nanocomposite.

### 3.3.4 Calcination

The Se/OP- nanocomposite was calcined at 550 °C in muffle furnace for 3 hours. The obtained product was expressed as Se/OP nanocomposite and placed in a desiccator for further use in experiment.

## 3.4. Characterization of Activated, Non-activated orange peels and Nanocomposite

The morphology and elements percentage of nano-composite was measured by using SEM (scanning electron microscopy), XRD (X-ray diffraction) and FT-IR (Fourier transform infrared spectroscopy) that was performed to explore the functional groups present in the sample.

### 3.4.1. Scanning Electron Microscopy (SEM)

SEM is an analytical method that yield high resolution duplicate image of samples by using focused beam of electrons as small as 15 nanometers. SEM provides three dimensional appearance of sample images that is beneficial while investigating the surface morphology of a sample. It is used to examine the morphology of sample. It produces images to collect data about composition and morphology of samples.

### 3.4.2. Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR is a technique that was performed to characterize activated as well as non-activated samples of orange peels, nanoparticles of selenium and nanocomposite of selenium and orange peels. It is a technique performed to attain infrared spectrum of absorption and emission of samples. FTIR analysis recognize organic as well as inorganic materials by scanning them through using infrared light. It is used for the detection of different functional groups. FTIR spectrum is recorded between 4000 and 400  $\text{cm}^{-1}$  as wave numbers.

### 3.4.3. X-Ray Diffraction (XRD)

XRD is a systematic testing method that was performed to identify and characterize the material crystallinity. For best results sample material is prepared as finely grounded material, homogenized and presented to the X-ray beam to determine the composition of sample. It is used to identify crystalline material and for quantitative determination of impurities in crystals. Another significant use of XRD is particle size determination. This analytical method is nondestructive and provides information on the molecular structure of the sample.

### 3.5.0. Batch Adsorption Experiment

The Se/orange peel Nanocomposite was applied as bio-sorbent to synthetic wastewater containing selected heavy metals (Pb and Cr) during series of batch experiment under variable parameters of pH, temperature, initial metal ion concentration and dose of adsorbent at a shaking speed of 100rpm and contact time of 60 minutes.

### **3.5.1. Synthesis of Wastewater containing Lead and Chromium**

For synthesis of wastewater containing selected heavy metals stock solutions of lead (Pb) and potassium chromate ( $K_2CrO_4$ ) were prepared in 100ml distilled water. Working solutions having concentration of 10ppm and 20ppm were prepared through dilution of both of the standard solutions (stock). The solution pH were settled by using drops of 1M HCl or 1M NaOH solution. Then Atomic Absorption Spectrophotometer was used for the analysis of concentration of Pb and Cr in prepared solutions.

### **3.5.2 Batch Adsorption Experiment**

The Se/OP nano composite was applied as bio-sorbent to synthetic wastewater samples (containing Pb and Cr) during series of batch experiment under variable parameters of pH, temperature, initial metal ion concentration, , adsorbent dose and contact time at 100 rpm.

### **3.5.3. Batch as a function of Initial Concentration**

In this experiment initial (primary) metal ion concentration of adsorbate (heavy metals) solution was varied while adsorbent dose and pH were kept constant. Adsorbate solutions were prepared having concentration of 10ppm and 20ppm and Se/orange peels nanocomposite was added as an adsorbent dose and placed in a vibrator (HY-4A CYCLING) at 100rpm for 90 minutes. The aliquot was drawn at 0min, 30min and 70min. Each aliquot was then filtered through filter paper. The concentration adsorbed was determined from calibration curve constructed with standards by running each filtrate on Atomic Adsorption Spectrophotometer (AAS).

### **3.5.4. Batch as a function of pH**

50ml of adsorbate solutions having concentration of 10ppm and 20ppm for lead and chromium were prepared in a beaker separately. The adsorbent dose of 0.5g and 0.10g were added in adsorbate solution while the pH of solution was settled by using diluted HCl or NaOH solution drop wise with the help of pH meter. The beakers containing the solutions were placed in a vibrator at 100rpm for 90min. Each filtrate was run on Atomic Adsorption Spectrophotometer. (AA-7000, SHIMADZU).

**3.5.5. Batch as a function of Adsorbent Dose**

50ml adsorbate solutions for both lead and Chromium with initial concentration of 10ppm and 20ppm were prepared where adsorbent dose was varied as 0.5g and 0.10g. The solutions were then placed in a vibrator at 100rpm for 90min. Each filtrate was run on Atomic Adsorption Spectrophotometer.

**3.5.6 Batch as a function of Temperature**

50ml of adsorbate solutions for both lead and chromium were prepared with initial concentration of 10ppm and 20ppm having adsorbent weight as 0.5g and 0.10g. Each sample was then treated with the temperature of 45°C and 60°C for 90min in water bath. The aliquot was drawn at 0min, 30min and 90min for both temperatures and each filtrate was run on Atomic Adsorption Spectrophotometer.

**CHAPTER #4**  
**RESULTS AND DISCUSSIONS**

## 4.0. Results and Discussions

The purpose of this contemporary study is to focus on the elimination of selected heavy metals (lead and chromium) from artificially synthesized waste water by means of low cost nano-composite (Se/Orange peel).

### 4.1. Characterization of Adsorbent

For characterization of the samples scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) analysis were performed.

#### 4.1.1. Scanning Electron Microscopy (SEM) Analysis

The SEM investigation was performed to characterize the surface morphology of the synthesized Nano-composite, activated and non-activated orange peels. SEM imaging of samples before (Non-activated Orange peels) and after treatment is represented in figure 3(a) and figure 3 (b) respectively. The characterization results in both figures showed that there is a significant change in morphology of orange peel before and after activation. From figure 3 (a) it is clear and obvious that orange peel has smooth surface before activation, while figure 3 (b) represented the morphology of Se/OP nano-composite which showed that it contains irregular intercellular spacing and pores which are formed due to the NaOH activation of activated carbon. These resulted outcomes were compared with previous literature which confirmed the successful adsorption through orange peel nano-composite as it is evident from results that carbon surface is extremely porous in nature. The pores present on the surface enhance the contact area during adsorption (Tay et al., 2009). So according to Rangabhashiyam et al., for efficient biosorption an internal surface, pores and spacing is necessary (Rangabhashiyam et al., 2014).

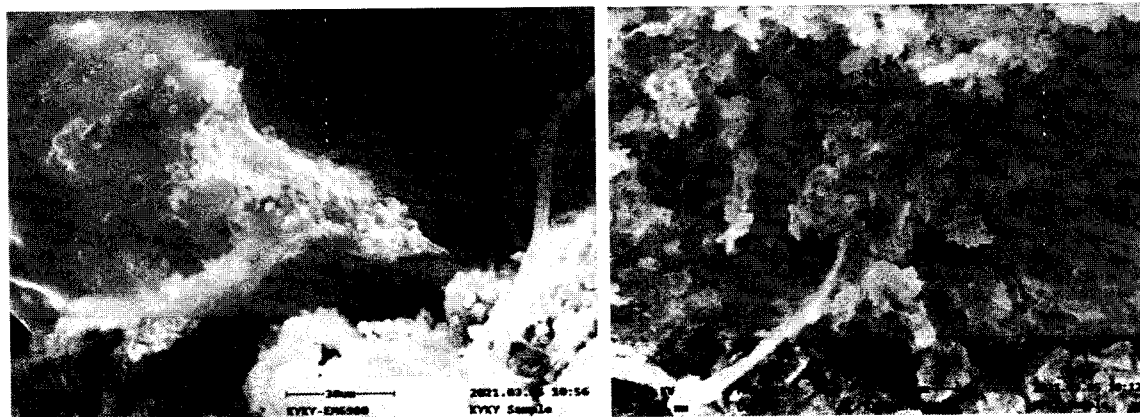


Figure 3 (a): Orange peel before activation and (b): Activated OP with Se/NPs as a Nanocomposite

#### 4.1.2. Fourier Transform Infrared Spectroscopy (FT-IR)

To investigate and define various functional groups attached with surface of the adsorbent for adsorbate binding, a standardized technique (FT-IR) was used to characterize activated, non-activated orange peels and Selenium nanocomposite sample. Functional groups on the surface of adsorbent can be identified effectively by FT-IR (Badmus et al., 2007).

Figure 5 showed the FT-IR spectrum of activated, non-activated orange peels samples and nanoparticles of Selenium which indicate the functional groups in synthesis and activation. The peak obtained at  $3550\text{cm}^{-1}$  is due to  $-\text{OH}$  stretching vibration, peak at  $2830\text{cm}^{-1}$  is may be due to  $-\text{CH}$  stretching vibration which is very strong. The band at  $2361\text{cm}^{-1}$  is may be the  $-\text{CH}$  stretch of aryl acid. The peak obtained at  $1630\text{cm}^{-1}$  is the indication of presence of  $\text{C}=\text{O}$  stretch of an aromatic ring, while the peak obtained at  $1190\text{cm}^{-1}$  represent  $\text{C}-\text{O}$  stretching vibration (Prasad et al., 2013). According to the research done for the adsorptive removal of heavy metal ions from industrial effluents by using activated carbon produced from coconut waste, the presence of  $\text{C}=\text{O}$  is the evidence for good adsorption properties associated with adsorbent that can coordinate with heavy metals. The presence of all the above mentioned functional groups were matched with referenced paper (Mallikarjuna et al., 2011) which confirmed the successful elimination (adsorption) of heavy metals by using Se/OP Nano-composite.

Table 4: FT-IR Spectral peaks, intensity and representative Functional Groups in Non-activated and Activated Se/OP Nano-composite.

| Peaks                 | Functional Groups   | Type of vibration | Intensity |
|-----------------------|---------------------|-------------------|-----------|
| 3644 $\text{cm}^{-1}$ | O-H (Alcohols)      | Stretched bonded  | Strong    |
| 2897 $\text{cm}^{-1}$ | C-H (Aldehyde)      | Stretched bonded  | Strong    |
| 2361 $\text{cm}^{-1}$ | C-H (Aryl acid)     | Stretched bonded  | Strong    |
| 1642 $\text{cm}^{-1}$ | C=C (Aromatic ring) | Stretched bonded  | Variable  |
| 1075 $\text{cm}^{-1}$ | C-O (Ester)         | Stretched bonded  | Strong    |

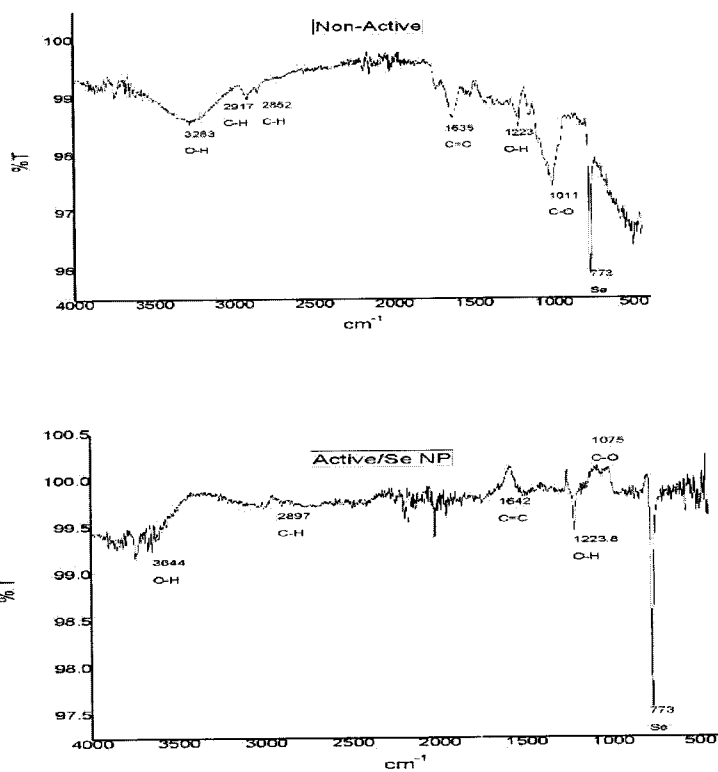


Figure 5 (a): FT-IR spectra of Orange peel before activation and (b) Activated orange peel with Se as a Nanocomposite

### 4.1.3. X-Ray Diffraction (XRD)

The XRD analysis was performed to analyze the configuration and composition of activated, non-activated orange peels and synthesized Selenium nanocomposite. Figure 6 showed the XRD spectra of Se nanoparticles, activated orange peels with Se as a nanocomposite and non-activated Orange peels. The XRD graph showed that there is a significant change in the structure before and after activation i.e. development of sharp peaks. These results showed that activated carbon was amorphous.

These results were compared with previous research that was done for the adsorption of chlorophenoxyacetic acid herbicides from water through activated carbon derived from coconut shell (Kasaoka et al., 1989) from which the idea of using Se/OP as a Nano-composite for adsorptive removal of heavy metals was raised as it is abundantly present in agricultural countries. The development of sharp peaks in the resulted spectrum obtained suggested good crystallinity of Se/OP Nano-composite as according to Ghada and Bahig for effective adsorption crystalline nature of the adsorbent is an important factor (Ghada and Bahig 2015).

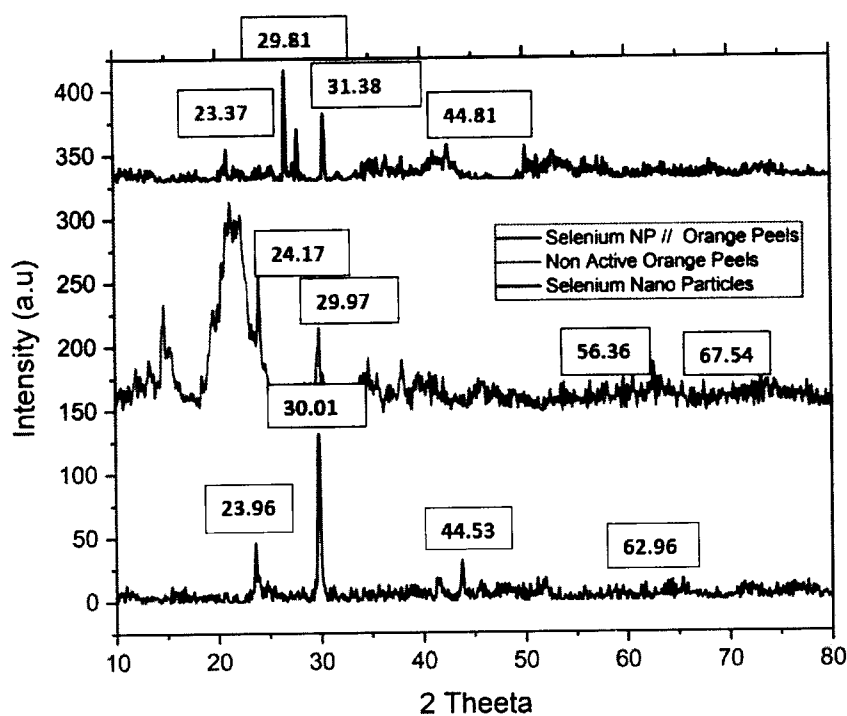


Figure 6: XRD spectra of Non activated orange peels and activated orange peels with Se as a Nanocomposite

## 4.2. Batch Adsorption Experiment

Different batch experiments were performed to examine the removal efficiency (adsorption) of the Se/OP Nano-composite. Series of batch experiments were conducted for each heavy metal separately to examine the effect of varying pH, effect of adsorbent dose, initial concentration (heavy metal), temperature and contact time.

### 4.2.1. Effect of pH

The pH of waste water is a significant key controlling parameter that governs adsorption of toxic substances from wastewater because it has the ability to effect concentration of counter ions present on functional groups of adsorbent as well as on the degree of ionization of adsorbate throughout the reaction (Nuhoglu et al., 2003).

In this current research study an experiment was conducted at two different pH i.e. pH 4 and pH 9 to study the influence of pH on the adsorption of selected heavy metals i.e. Lead and Chromium. The process of adsorption was rapid in both acidic and basic pH but more in acidic for both Pb and Cr. The % removal of Cr at 10ppm was best at acidic pH while at 20ppm the %removal was best at basic pH.

The % removal of Pb was maximum at both acidic and basic pH but increased as the pH concentration changed from 4 to 9. The increase in %removal with increasing pH may be explained by the fact that hydrogen ions in the solution reduced and the struggle and competition for metals and hydrogen ions for active sites of adsorbent also reduces which consequently leads to increase in metal removal (Gueye et al., 2014). Because of metal precipitation from solution in the form of  $H^+$  for pH values more than 6.0, so it usually leads maximum removal at neutral pH and pH 9 (Taffarel and Rubio, 2009). From present study it is evident that adsorption of Pb and Cr by Se/OP nano-composite was significantly affected by pH.

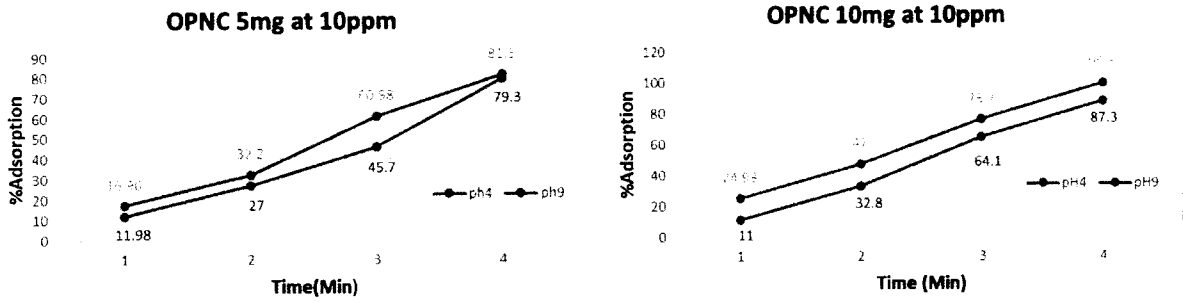


Figure: 7 Removal (%) of 10ppm Cr on OPNC at 5mg and 10mg as a function of pH at variable contact time

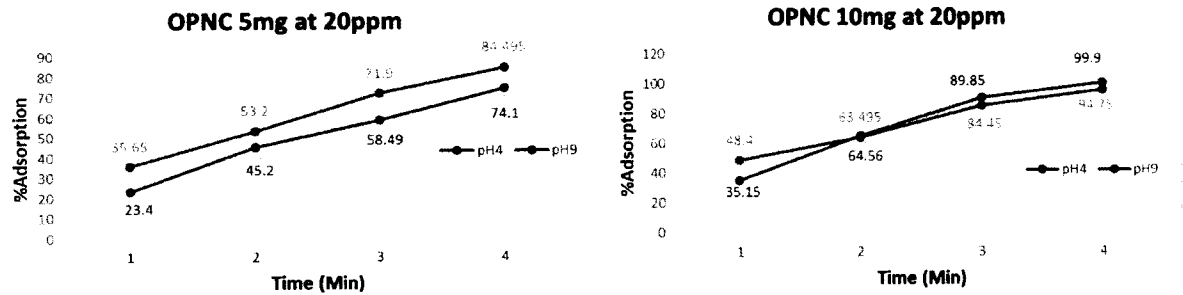


Figure: 8 Removal (%) of 20ppm Cr on OPNC at 5mg and 10mg as a function of pH at variable contact time

Table: 5 Removal (%) of Lead by Nano-composite at variable pH

| Time            | 10ppm |       |       |       |
|-----------------|-------|-------|-------|-------|
|                 | 5mg   |       | 10mg  |       |
|                 | pH4   | pH9   | pH4   | pH9   |
| Initial contact | 68.98 | 59.89 | 69.88 | 59.86 |
| 30              | 79.86 | 69.23 | 88.87 | 73.84 |
| 60              | 88.70 | 84.90 | 89.99 | 86.88 |
| 90              | 98.80 | 89.61 | 99.88 | 98.97 |

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|                 |       | 20ppm |       |       |
|-----------------|-------|-------|-------|-------|
| Initial contact | 69.44 | 74.66 | 74.49 | 79.43 |
| 30              | 74.10 | 83.84 | 84.46 | 84.42 |
| 60              | 89.25 | 89.39 | 85.89 | 94.74 |
| 90              | 94.93 | 99.88 | 96.69 | 99.99 |

#### 4.2.2 Effect of Adsorbent Dose

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Adsorbent dosage is a key important factor for controlling the availability and accessibility of adsorption sites (Rafeah et al., 2009). In the current study in order to examine the effect and consequence of adsorbent dose, varying doses of adsorbent (5mg and 10mg) were used for both Pb and Cr. According to the results shown in figure 9 it is evident that as the adsorbent dose increased the % removal of adsorbate also increased while when both adsorbate concentration and adsorbent dose increase together, the % removal also increase as shown in figure 10. Hence on the basis of these results it can be concluded that Se/OP Nano-composite has unique adsorption capacity because of maximum removal off 99.4% at the dose of 10mg for 20ppm concentration of adsorbate (Heavy metals).

Gangadhar also studied the influence of adsorbent dose for the adsorption of both Malathion and Phorate which showed that adsorption capacity was increased as adsorbate concentration increased (Gangadhar et al., 2016). As the amount of adsorbent increased it will definitely enhances the number of sites for adsorption and ultimately increase the adsorbent surface area (Sulyman et al., 2016) which supported the maximum adsorption capacity of Se/OP Nano-composite as represented below.

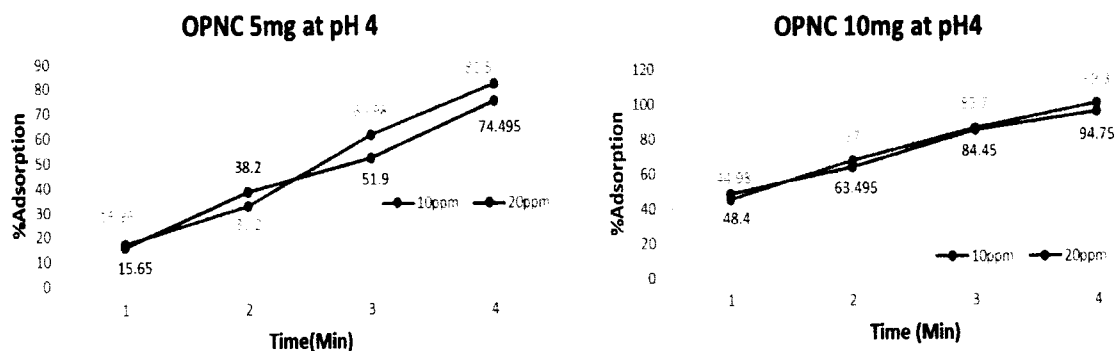


Figure: 9 Removal (%) 10ppm and 20ppm Cr on 5mg and 10mg OPNC at pH4 as a function of adsorbent dose at variable contact time

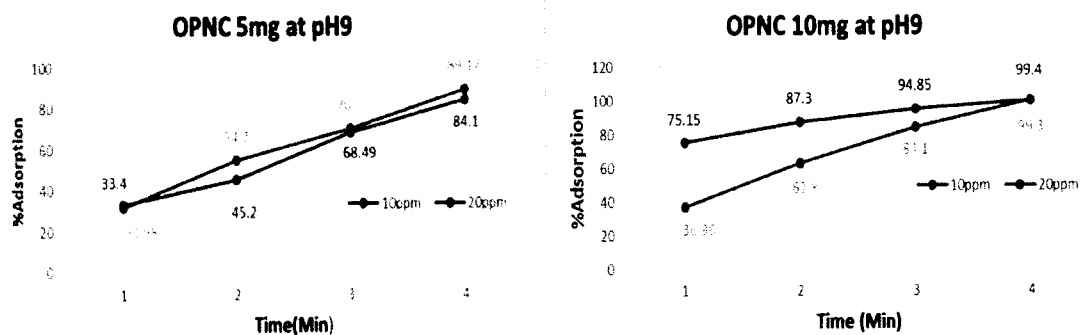


Figure: 10 Removal (%) 10ppm and 20ppm Cr on 5mg and 10mg OPNC at pH9 as a function of adsorbent dose at variable contact time

Table: 6 Removal of Pb by Nano-composite at variable dose and initial concentration

|                 | 5mg   |       |       |       |
|-----------------|-------|-------|-------|-------|
| Time            | pH4   | pH9   |       |       |
|                 | 10ppm | 20ppm | 10ppm | 20ppm |
| Initial contact | 58.98 | 54.40 | 59.89 | 59.51 |
| 30              | 69.86 | 59.12 | 69.23 | 68.84 |
| 60              | 88.79 | 84.25 | 84.91 | 80.39 |
| 90              | 99.86 | 94.43 | 89.61 | 89.38 |

|                 |       | 10mg  |       |       |
|-----------------|-------|-------|-------|-------|
| Initial contact | 69.88 | 84.49 | 49.86 | 79.43 |
| 30              | 88.87 | 89.46 | 63.84 | 84.42 |
| 60              | 89.99 | 90.89 | 76.88 | 94.74 |
| 90              | 97.69 | 99.88 | 88.97 | 98.46 |

### 4.2.3. Effect of Temperature

In this present study in order to examine and evaluate the effect of temperature on the efficiency of adsorption, varied temperature were used i.e. 45°C and 60°C for both Pb and Cr at different time intervals. The results given in figure 12 and table 7 showed that by increasing the temperature the % removal of metals increases as well. Moreover as the adsorbate concentration and adsorbent dose increase together, the % removal (adsorption) also increases as shown below. Hence the optimum dose is 10mg, optimum temperature is 60°C at concentration of 20ppm for both lead and chromium because of maximum removal of about 98.3% for lead and 95.93% for Chromium. The results showed that temperature was most effective parameter for heavy metal adsorption. At higher temperatures the adsorption capacity of OPAC increased may be due to high porosity and large surface area. This current investigation is compared with previous literature i.e. the dye removal from aqueous solution using polymer composite films, where the adsorption increased in the same pattern as mentioned above (Robati et al., 2016). So it can be concluded that OPAC is an effective and promising material for heavy metal adsorption from wastewater as it is abundantly available in large amounts. So it is concluded that orange peel waste is very effective, low cost adsorbent, easily available in large amounts and has maximum removal efficiency due which it was an effective step to use this waste by doping with nanoparticles to enhance the removal efficiency in a very less time and also it does not required large infrastructure.

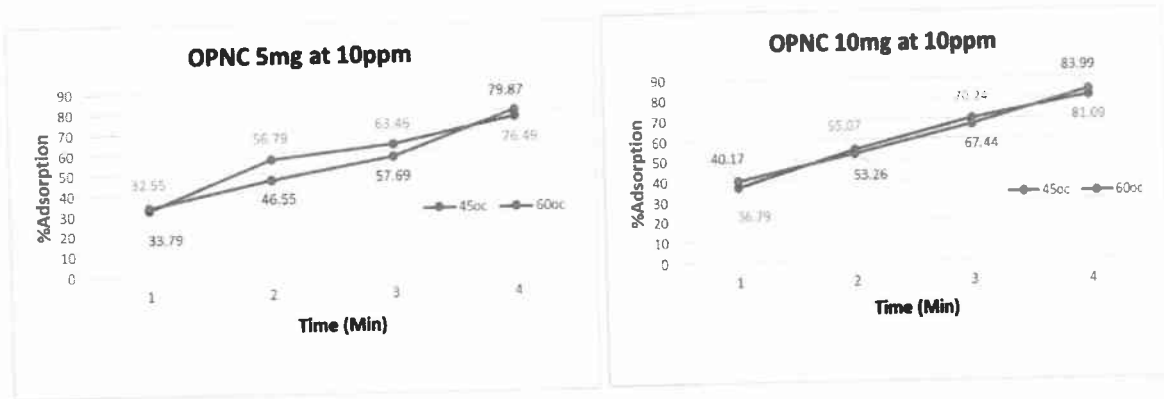


Figure: 11 Removal (%) of 10ppm Cr on OPNC at 5mg and 10mg as a function of Temperature at variable contact time

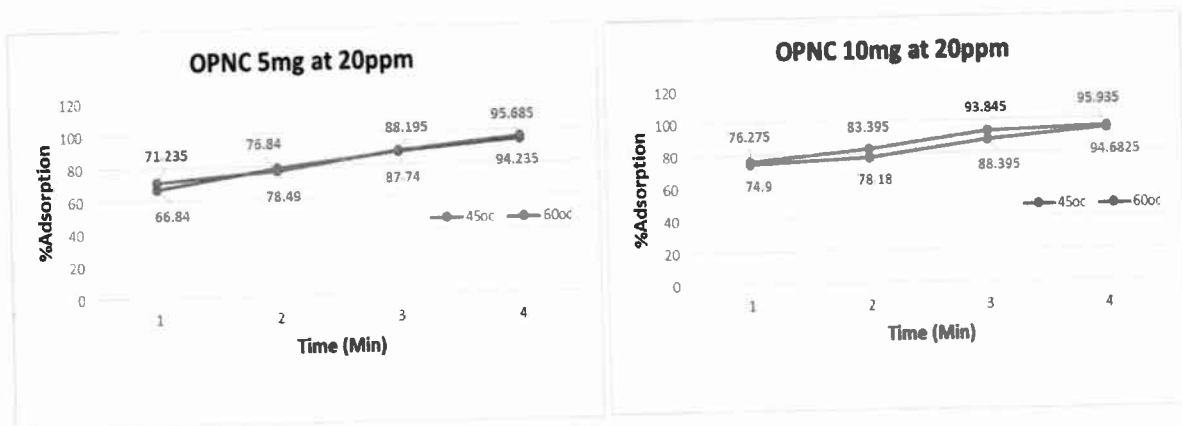


Figure: 12 Removal (%) of 20ppm Cr on OPNC at 5mg and 10mg as a function of Temperature at variable contact time

Table: 7 Removal (%) of Lead by Nano-composite at variable temperature

| Time            | 10ppm  |        |       |       |
|-----------------|--------|--------|-------|-------|
|                 | 5mg    |        | 10mg  |       |
|                 | 45°C   | 60°C   | 45°C  | 60°C  |
| Initial contact | 36.75  | 26.79  | 47.86 | 46.88 |
| 30              | 49.688 | 40.69  | 69.68 | 57.69 |
| 60              | 66.59  | 65.48  | 78.8  | 63.88 |
| 90              | 89.09  | 79.058 | 89.89 | 71.87 |
|                 |        | 20ppm  |       |       |

|                 |        |        |        |        |
|-----------------|--------|--------|--------|--------|
| Initial contact | 55.64  | 62.895 | 63.395 | 73.395 |
| 30              | 70.545 | 74.38  | 75.695 | 81.44  |
| 60              | 83.395 | 82.395 | 87.395 | 93.73  |
| 90              | 90.145 | 93.745 | 95.895 | 98.395 |

#### 4.2.4. Effect of Initial Concentration

In this experiment the adsorption study for the removal of Pb and Cr was carried out at initial concentration of 10ppm and 20ppm to determine the influence of initial concentration on the efficiency of adsorption (heavy metals i.e. Pb and Cr) using Se/OP Nano-composite. According to the experimental results given in figure 7, figure 8 and table 5 it is evident that percentage adsorption increased by decreasing initial concentration. It is also concluded from the given results that adsorption capacity improved by increasing adsorbent dose along with increase in adsorbate concentration because of increase in number of adsorbent sites and of the adsorbate particles.

These results were compared with previous research i.e. Gupta, 2015 examined the effect of initial concentration where the concentration of sorbate was varied over the range of 10-50mg/L in the presence of 10mg of adsorbent. In this research study it was observed that by increasing the concentration of sorbate the adsorption efficiency of phenanthrene was increased (Gupta, 2015).

The adsorption capacity also increases by increasing initial concentration (10ppm and 20ppm) of heavy metals just because of lower ratio of initial number of metal ions to the available surface area at low concentration and vice versa, therefore the removal of heavy metals depends upon concentration as well (Bakka et al., 2016).

#### 4.2.5. Effect of Contact Time

The adsorption study was carried out at different parameters (5-10mg adsorbent dose, 10-20ppm initial metal ion concentration, pH 4-9 at the speed of 100rpm with varying contact time) to investigate the elimination of selected heavy metals i.e. Pb and Cr from aqueous solution of synthetic wastewater. Therefore effect of contact time was investigated over the range of 0-90 minutes for both Pb and Cr.

On the basis of investigated results it is evident that the percentage removal increased by increasing the contact time that might be due to accessibility of more active sites on the surface of adsorbent. Hence optimal interaction time for the elimination of both Pb and Cr was observed at 90min because the contact time was independent of metal ion concentration for the maximum removal by activated carbon.

# **CHAPTER #5**

## **CONCLUSIONS**

### 5.0. Conclusion

The present study aimed to investigate the adsorption capacity of Se/OP Nano-composite. In this investigation activated carbon was synthesized from orange peels for the elimination of Pb and Cr through the process of adsorption. The characteristics of adsorbent can be determined by its physical and chemical properties.

From batch experiments it is concluded that adsorption capacity can be influenced by various factors including pH, temperature, and concentration of heavy metals, adsorbent dose, and contact time. From experimental results it is concluded that activated carbon produced from Orange peels is an encouraging and favorable adsorbent for the elimination of Pb and Cr.

Orange peels is discarded, inexpensive and abundantly available in agricultural countries, so this study provides an evidence that Orange peel doped with nano-particles is cost effective and suitable natural adsorbent for the elimination of pollutants and heavy metals from contaminated wastewater or effluents.

## **REFERENCES**

- Abdel-Raouf, M. S., & Abdul-Raheim, A. R. M. (2017). Removal of Heavy Metals from Industrial Waste Water by Biomass-Based Materials: A Review. *J Pollut Eff Cont* 5: 180. doi: 10.4172/2375-4397.1000180 Page 2 of 13 Volume 5• Issue 1• 1000180 *J Pollut Eff Cont*, an open access journal ISSN: 2375-4397 The Top Six Toxic Threats: Estimated Population at risk at Identified Sites\*(million people) Estimated Global Impact\*\*(million people) 1. Lead 10 18-22 2. *Mercury*, 8, 15-19.
- Achar, K. C., Hosamani, K. M., & Seetharamareddy, H. R. (2010). In-vivo analgesic and anti-inflammatory activities of newly synthesized benzimidazole derivatives. *European journal of medicinal chemistry*, 45(5), 2048-2054.
- Agins, H. J., Alcock, N. W., Bansal, M., Salvati, E. A., Wilson, P. D., Pellicci, P. M., & Bullough, P. G. (1988). Metallic wear in failed titanium-alloy total hip replacements. *J Bone Joint Surg*, 70(3), 347-356.
- Ahmed, S. I., Johari, A., Hashim, H., Lim, J. S., Jusoh, M., Mat, R., & Alkali, H. (2015). Economic and environmental evaluation of landfill gas utilisation: A multi-period optimisation approach for low carbon regions. *International Biodeterioration & Biodegradation*, 102, 191-201.
- Ajmi, R. N., Sultan, M., & Hanno, S. H. (2018). Bioabsorbent of Chromium, Cadmium and Lead from Industrial waste water by Waste plant. *Journal of Pharmaceutical Sciences and Research*, 10(3), 672-674.
- Al-Qahtani, K. M. (2016). Water purification using different waste fruit cortexes for the removal of heavy metals. *Journal of Taibah University for science*, 10(5), 700-708.
- Anirudhan, T. S., & Sreekumari, S. S. (2011). Adsorptive removal of heavy metal ions from industrial effluents using activated carbon derived from waste coconut buttons. *Journal of Environmental Sciences*, 23(12), 1989-1998.
- Aral, A., & Gupta, V. (2016). Direct estimates for Lupaş-Durrmeyer operators. *Filomat*, 30(1), 191-199.
- Asfaram, A., Ghaedi, M., Azqhandi, M. H. A., Goudarzi, A., & Hajati, S. (2017). Ultrasound-assisted binary adsorption of dyes onto Mn@ CuS/ZnS-NC-AC as a novel adsorbent: application of chemometrics for optimization and modeling. *Journal of industrial and engineering chemistry*, 54, 377-388.

- Babel, S., & Kurniawan, T. A. (2004). Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere*, 54(7), 951-967.
- Bao, H., Pan, Y., Ping, Y., Sahoo, N. G., Wu, T., Li, L., & Gan, L. H. (2011). Chitosan-functionalized graphene oxide as a nanocarrier for drug and gene delivery. *Small*, 7(11), 1569-1578.
- Baroni, L., Cenci, L., Tettamanti, M., & Berati, M. (2007). Evaluating the environmental impact of various dietary patterns combined with different food production systems. *European journal of clinical nutrition*, 61(2), 279-286.
- Badmus, M. A. O., Audu, T. O. K., & Anyata, B. U. (2007). Removal of lead ion from industrial wastewaters by activated carbon prepared from periwinkle shells (*Typanotonus fuscatus*). *Turkish journal of engineering and environmental sciences*, 31(4), 251-263.
- Baseri, J. R., Palanisamy, P. N., & Sivakumar, P. (2012). Preparation and characterization of activated carbon from *Thevetia peruviana* for the removal of dyes from textile waste water. *Advances in Applied Science Research*, 3(1), 377-383.
- Ben-Ali, S., Jaouali, I., Souissi-Najar, S., & Ouederni, A. (2017). Characterization and adsorption capacity of raw pomegranate peel biosorbent for copper removal. *Journal of Cleaner Production*, 142, 3809-3821.
- Buasri, A., Chaiyut, N., Tapang, K., Jaroensin, S., & Panphrom, S. (2012). Equilibrium and kinetic studies of biosorption of Zn (II) ions from wastewater using modified corn cob. *Apchee Procedia*, 3, 60-64.
- Bakka, H., Vanhatalo, J., Illian, J., Simpson, D., & Rue, H. (2016). Accounting for physical barriers in species distribution modeling with non-stationary spatial random effects. *arXiv preprint arXiv:1608.03787*.
- Buasri, A., Chaiyut, N., Tapang, K., Jaroensin, S., & Panphrom, S. (2012). Equilibrium and kinetic studies of biosorption of Zn (II) ions from wastewater using modified corn cob. *Apchee Procedia*, 3, 60-64.
- Bunani, S., Yörükoğlu, E., Yüksel, U., Kabay, N., Yüksel, M., & Sert, G. (2015). Application of reverse osmosis for reuse of secondary treated urban wastewater in agricultural irrigation. *Desalination*, 364, 68-74.

- Cay, S., Uyanık, A., & Özaşık, A. (2004). Single and binary component adsorption of copper (II) and cadmium (II) from aqueous solutions using tea-industry waste. *Separation and purification technology*, 38(3), 273-280.
- Chaukura, N., Murimba, E. C., & Gwenzi, W. (2017). Synthesis, characterisation and methyl orange adsorption capacity of ferric oxide–biochar nano-composites derived from pulp and paper sludge. *Applied Water Science*, 7(5), 2175-2186.
- Chen, J. Q., Meng, X. P., Zhang, Y., Xia, M., & Wang, X. P. (2008). Over-expression of OsDREB genes lead to enhanced drought tolerance in rice. *Biotechnology letters*, 30(12), 2191-2198.
- Choong, E. T., & Achmadi, S. S. (2007). Effect of extractives on moisture sorption and shrinkage in tropical woods. *Wood and Fiber science*, 23(2), 185-196.
- Chung, M. K., Kim, H. J., Lee, Y. S., Han, M. E., Yoon, S., Baek, S. Y., & Oh, S. O. (2010). Hedgehog signaling regulates proliferation of prostate cancer cells via stathmin1. *Clinical and experimental medicine*, 10(1), 51-57.
- Cingolani, P., Platts, A., Wang, L. L., Coon, M., Nguyen, T., Wang, L., & Ruden, D. M. (2012). A program for annotating and predicting the effects of single nucleotide polymorphisms, SnpEff: SNPs in the genome of *Drosophila melanogaster* strain w1118; iso-2; iso-3. *Fly*, 6(2), 80-92.
- Cingolani, P., Platts, A., Wang, L. L., Coon, M., Nguyen, T., Wang, L., & Ruden, D. M. (2012). A program for annotating and predicting the effects of single nucleotide polymorphisms, SnpEff: SNPs in the genome of *Drosophila melanogaster* strain w1118; iso-2; iso-3. *Fly*, 6(2), 80-92.
- Corcho-Corral, B., Olivares-Marín, M., Fernandez-Gonzalez, C., Gomez-Serrano, V., & Macías-García, A. (2006). Preparation and textural characterisation of activated carbon from vine shoots (*Vitis vinifera*) by H<sub>3</sub>PO<sub>4</sub>—chemical activation. *Applied Surface Science*, 252(17), 5961-5966.
- D'Arrigo, R., & Wilson, R. (2006). On the Asian expression of the PDO. *International Journal of Climatology: A Journal of the Royal Meteorological Society*, 26(12), 1607-1617.

- Demirbaş, E., Kobyay, M., Öncel, S., & Şencan, S. (2000). Removal of Ni (II) from aqueous solution by adsorption onto hazelnut shell activated carbon: equilibrium studies. *Bioresource technology*, 84(3), 291-293.
- Di Lazzaro, V., Pilato, F., Saturno, E., Oliviero, A., Dileone, M., Mazzone, P., & Rothwell, J. C. (2005). Theta-burst repetitive transcranial magnetic stimulation suppresses specific excitatory circuits in the human motor cortex. *The Journal of physiology*, 565(3), 945-950.
- Di Natale, F., Erto, A., Lancia, A., & Musmarra, D. (2009). A descriptive model for metallic ions adsorption from aqueous solutions onto activated carbons. *Journal of hazardous materials*, 169(1-3), 360-369.
- Dil, E. A., Ghaedi, M., & Asfaram, A. (2017). The performance of nanorods material as adsorbent for removal of azo dyes and heavy metal ions: application of ultrasound wave, optimization and modeling. *Ultrasonics Sonochemistry*, 34, 792-802.
- Dresselhaus, M. S., & Terrones, M. (2013). Carbon-based nanomaterials from a historical perspective. *Proceedings of the IEEE*, 101(7), 1522-1535.
- El-Said, A. G., Gamal, A. M., & Mansour, H. F. (2013). Potential application of orange peel as an eco-friendly adsorbent for textile dyeing effluents. *Research Journal of Textile and Apparel*.
- Engelsma, M. Y., Way, K., Dodge, M. J., Voorbergen-Laarman, M., Panzarin, V., Abbadi, M., ... & Stone, D. M. (2013). Detection of novel strains of cyprinid herpesvirus closely related to koi herpesvirus. *Diseases of Aquatic Organisms*, 107(2), 113-120.
- Gueye, M., Richardson, Y., Kafack, F. T., & Blin, J. (2014). High efficiency activated carbons from African biomass residues for the removal of chromium (VI) from wastewater. *Journal of Environmental Chemical Engineering*, 2(1), 273-281.
- Gangadhar, B. H., Sajeesh, K., Venkatesh, J., Baskar, V., Abhinandan, K., Yu, J. W., ... & Mishra, R. K. (2016). Enhanced tolerance of transgenic potato plants over-expressing non-specific lipid transfer protein-1 (StnsLTP1) against multiple abiotic stresses. *Frontiers in Plant Science*, 7, 1228.
- Gangadhar, B., Tharakeswar, Y., Kalyan, Y. and Naidu, G., R. (2016), Tea (*Camellia sinensis*) Waste for the reduction of Malathion and Phorate in aqueous solutions,

- International Journal of Environmental & Agriculture Research (IJOEAR), 2(6), 2454-1850.
- Garg, V. K., Amita, M., Kumar, R., & Gupta, R. (2004). Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste. *Dyes and pigments*, 63(3), 243-250.
  - Goldstein, J. A., Rothman, M., & Lo, W. Y. (2012). *U.S. Patent No. 8,232,304*. Washington, DC: U.S. Patent and Trademark Office.
  - Gupta, V. K., & Nayak, A. (2012). Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe<sub>2</sub>O<sub>3</sub> nanoparticles. *Chemical engineering journal*, 180, 81-90.
  - Gupta, V. K., Agarwal, S., & Saleh, T. A. (2011). Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal. *Journal of hazardous materials*, 185(1), 17-23.
  - Gupta, V. K., Moradi, O., Tyagi, I., Agarwal, S., Sadegh, H., Shahryari-Ghoshekandi, R., ... & Garshasbi, A. (2016). Study on the removal of heavy metal ions from industry waste by carbon nanotubes: effect of the surface modification: a review. *Critical Reviews in Environmental Science and Technology*, 46(2), 93-118.
  - Gupta, V. K., Nayak, A., Agarwal, S., Gupta, V. K., Nayak, A., & Agarwal, S. (2015). Bioadsorbents for remediation of heavy metals: current status and their future prospects. *Environmental engineering research*, 20(1), 1-18.
  - Hossain, M. A., Ngo, H. H., Guo, W. S., & Setiadi, T. (2012). Adsorption and desorption of copper (II) ions onto garden grass. *Bioresource technology*, 121, 386-395.
  - Hossain, M. A., Piyatida, P., da Silva, J. A. T., & Fujita, M. (2012). Molecular mechanism of heavy metal toxicity and tolerance in plants: central role of glutathione in detoxification of reactive oxygen species and methylglyoxal and in heavy metal chelation. *Journal of Botany*, 2012.
  - Hussein, H., Ibrahim, S. F., Kandeel, K., & Moawad, H. (2004). Biosorption of heavy metals from waste water using *Pseudomonas* sp. *Electronic journal of Biotechnology*, 7(1), 30-37.

- Igwe, J. C., & Abia, A. A. (2007). Adsorption isotherm studies of Cd (II), Pb (II) and Zn (II) ions bioremediation from aqueous solution using unmodified and EDTA-modified maize cob. *Eclética Química*, 32(1), 33-42.
- Jang, Y., & Gerhardt, H. C. (2006). Divergence in female calling song discrimination between sympatric and allopatric populations of the southern wood cricket *Gryllus fultoni* (Orthoptera: Gryllidae). *Behavioral Ecology and Sociobiology*, 60(2), 150-158.
- Jaouali, I., Hamrouni, H., Moussa, N., Nsib, M. F., Centeno, M. A., Bonavita, A., & Leonardi, S. G. (2018). LaFeO<sub>3</sub> ceramics as selective oxygen sensors at mild temperature. *Ceramics International*, 44(4), 4183-4189.
- Jinfeng, M. A., Li, T. A. N. G., Kaifeng, R. A. O., Gang, H. O. N. G., & Mei, M. A. (2019). Cluster computing mode for water environment simulation based on Hadoop. *Big Data Research*, 5(6), 73.
- Javed, M., & Usmani, N. (2013). Assessment of heavy metal (Cu, Ni, Fe, Co, Mn, Cr, Zn) pollution in effluent dominated rivulet water and their effect on glycogen metabolism and histology of *Mastacembelus armatus*. *SpringerPlus*, 2(1), 390.
- Joshi, S., Garg, V. K., Kataria, N., & Kadirvelu, K. (2019). Applications of Fe<sub>3</sub>O<sub>4</sub>@ AC nanoparticles for dye removal from simulated wastewater. *Chemosphere*, 236, 124280.
- Joss, A., Zabczynski, S., Göbel, A., Hoffmann, B., Löffler, D., McArde, C. S., ... & Siegrist, H. (2006). Biological degradation of pharmaceuticals in municipal wastewater treatment: proposing a classification scheme. *Water research*, 40(8), 1686-1696.
- Kanawade, S. M., & Gaikwad, R. W. (2011). Removal of methylene blue from effluent by using activated carbon and water hyacinth as adsorbent. *International Journal of Chemical Engineering and Applications*, 2(5), 317.
- Karthikeyan, T., Rajgopal, S., & Miranda, L. R. (2005). Chromium (VI) adsorption from aqueous solution by Hevea Brasilinesis sawdust activated carbon. *Journal of hazardous materials*, 124(1-3), 192-199.
- Karthikeyan, T., Rajgopal, S., & Miranda, L. R. (2005). Chromium (VI) adsorption from aqueous solution by Hevea Brasilinesis sawdust activated carbon. *Journal of hazardous materials*, 124(1-3), 192-199.

- Keirstead, J., Jennings, M., & Sivakumar, A. (2012). A review of urban energy system models: Approaches, challenges and opportunities. *Renewable and Sustainable Energy Reviews*, 16(6), 3847-3866.
- Khan, A. S., & Liu, H. (2012). Strain rate and temperature dependent fracture criteria for isotropic and anisotropic metals. *International Journal of Plasticity*, 37, 1-15.
- Khan, A. S., Yu, S., & Liu, H. (2012). Deformation induced anisotropic responses of Ti-6Al-4V alloy Part II: A strain rate and temperature dependent anisotropic yield criterion. *International Journal of Plasticity*, 38, 14-26.
- Khan, A. S., Yu, S., & Liu, H. (2012). Deformation induced anisotropic responses of Ti-6Al-4V alloy Part II: A strain rate and temperature dependent anisotropic yield criterion. *International Journal of Plasticity*, 38, 14-26.
- Kharisov, B. I., Dias, H. R., & Kharissova, O. V. (2014). Nanotechnology-based remediation of petroleum impurities from water. *Journal of Petroleum Science and Engineering*, 122, 705-718.
- Khatamian, M., Khodakarampoor, N., & Saket-Oskoui, M. (2017). Efficient removal of arsenic using graphene-zeolite based composites. *Journal of colloid and interface science*, 498, 433-441.
- Kobya, M. (2004). Removal of Cr (VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: kinetic and equilibrium studies. *Bioresource technology*, 91(3), 317-321.
- Korover, I., Muangma, N., Hen, O., Shneor, R., Sulkosky, V., Kelleher, A., ... & Jefferson Lab Hall A Collaboration. (2014). Probing the Repulsive Core of the Nucleon-Nucleon Interaction via the He 4 (e, e' p N) Triple-Coincidence Reaction. *Physical review letters*, 113(2), 022501.
- Kumar, K., Dasgupta, C. N., & Das, D. (2014). Cell growth kinetics of *Chlorella sorokiniana* and nutritional values of its biomass. *Bioresource technology*, 167, 358-366.
- Kurniawan, T. A., Chan, G. Y., Lo, W. H., & Babel, S. (2006). Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Science of the total environment*, 366(2-3), 409-426.

- Li, P., Lu, R. S., Xu, W. Q., Ohi-Toma, T., Cai, M. Q., Qiu, Y. X., & Fu, C. X. (2017). Comparative genomics and phylogenomics of East Asian tulips (*Amana*, Liliaceae). *Frontiers in plant science*, 8, 451.
- Lim, J. Y., Mubarak, N. M., Abdullah, E. C., Nizamuddin, S., & Khalid, M. (2018). Recent trends in the synthesis of graphene and graphene oxide based nanomaterials for removal of heavy metals—A review. *Journal of Industrial and Engineering Chemistry*, 66, 29-44.
- Liu, N. F., Liu, Q., Wang, L. Z., Liang, S. L., Wen, J. G., Qu, Y., & Liu, S. H. (2013). A statistics-based temporal filter algorithm to map spatiotemporally continuous shortwave albedo from MODIS data. *Hydrology and Earth System Sciences*, 17(6), 2121.
- Manivasagan, P., Venkatesan, J., Sivakumar, K., & Kim, S. K. (2014). Pharmaceutically active secondary metabolites of marine actinobacteria. *Microbiological research*, 169(4), 262-278.
- Manivasagan, P., Venkatesan, J., Sivakumar, K., & Kim, S. K. (2014). Pharmaceutically active secondary metabolites of marine actinobacteria. *Microbiological research*, 169(4), 262-278.
- Mantell, C. L. (1968). Carbon and Graphite Handbook.
- Maran, J. P., Sivakumar, V., Thirugnanasambandham, K., & Sridhar, R. (2013). Optimization of microwave assisted extraction of pectin from orange peel. *Carbohydrate polymers*, 97(2), 703-709.
- Martínez-Cabanas, M., López-García, M., Barriada, J. L., Herrero, R., & de Vicente, M. E. S. (2016). Green synthesis of iron oxide nanoparticles. Development of magnetic hybrid materials for efficient As (V) removal. *Chemical Engineering Journal*, 301, 83-91.
- Maynard, A. D., Baron, P. A., Foley, M., Shvedova, A. A., Kisin, E. R., & Castranova, V. (2004). Exposure to carbon nanotube material: aerosol release during the handling of unrefined single-walled carbon nanotube material. *Journal of Toxicology and Environmental Health, Part A*, 67(1), 87-107.
- Mezohegyi, G., van der Zee, F. P., Font, J., Fortuny, A., & Fabregat, A. (2012). Towards advanced aqueous dye removal processes: a short review on the versatile role of activated carbon. *Journal of environmental management*, 102, 148-164.

- Mohammadi, T., Reesink, H. W., Pietersz, R. N. I., Vandenbroucke-Grauls, C. M. J. E., & Savelkoul, P. H. M. (2005). Amplified-fragment length polymorphism analysis of *Propionibacterium* isolates implicated in contamination of blood products. *British journal of haematology*, 131(3), 403-409.
- Murphy, K. R., Hambly, A., Singh, S., Henderson, R. K., Baker, A., Stuetz, R., & Khan, S. J. (2011). Organic matter fluorescence in municipal water recycling schemes: toward a unified PARAFAC model. *Environmental science & technology*, 45(7), 2909-2916.
- Musico, Y. L. F., Santos, C. M., Dalida, M. L. P., & Rodrigues, D. F. (2013). Improved removal of lead (II) from water using a polymer-based graphene oxide nanocomposite. *Journal of Materials Chemistry A*, 1(11), 3789-3796.
- Malhotra, S., Jha, N., & Desai, K. (2014). A superficial synthesis of selenium nanospheres using wet chemical approach. *Int J Nanotechnol Appl*, 3, 7-14.
- Nuruzzaman, M. D., Rahman, M. M., Liu, Y., & Naidu, R. (2016). Nanoencapsulation, nano-guard for pesticides: a new window for safe application. *Journal of agricultural and food chemistry*, 64(7), 1447-1483.
- Nuhoglu, Y., & Oguz, E. (2003). Removal of copper (II) from aqueous solutions by biosorption on the cone biomass of *Thuja orientalis*. *Process Biochemistry*, 38(11), 1627-1631.
- Olaoye, R. A., Afolayan, O. D., Mustapha, O. I., & Adeleke, H. G. (2018). The Efficacy of Banana Peel Activated Carbon in the Removal of Cyanide and Selected Metals from Cassava Processing Wastewater. *Advances in Research*, 1-12.
- Olaoye, R. A., Afolayan, O. D., Mustapha, O. I., & Adeleke, H. G. (2018). The Efficacy of Banana Peel Activated Carbon in the Removal of Cyanide and Selected Metals from Cassava Processing Wastewater. *Advances in Research*, 1-12.
- Palanisamy, P., Yadav, V., & Elchuri, H. (2013, June). Serendio: Simple and Practical lexicon based approach to Sentiment Analysis. In *Second Joint Conference on Lexical and Computational Semantics (\* SEM), Volume 2: Proceedings of the Seventh International Workshop on Semantic Evaluation (SemEval 2013)* (pp. 543-548).
- Pandiarajan, A., Kamaraj, R., Vasudevan, S., & Vasudevan, S. (2018). OPAC (orange peel activated carbon) derived from waste orange peel for the adsorption of

- chlorophenoxyacetic acid herbicides from water: adsorption isotherm, kinetic modelling and thermodynamic studies. *Bioresource technology*, 261, 329-341.
- Park, E. J., Lee, J. H., Yu, G. Y., He, G., Ali, S. R., Holzer, R. G., ... & Karin, M. (2010). Dietary and genetic obesity promote liver inflammation and tumorigenesis by enhancing IL-6 and TNF expression. *Cell*, 140(2), 197-208.
  - Pollard, S. J. T., Fowler, G. D., Sollars, C. J., & Perry, R. (1992). Low-cost adsorbents for waste and wastewater treatment: a review. *Science of the total environment*, 116(1-2), 31-52.
  - Readman, J. W., Fillmann, G., Tolosa, I., Bartocci, J., Villeneuve, J. P., Catinni, C., & Mee, L. D. (2002). Petroleum and PAH contamination of the Black Sea. *Marine Pollution Bulletin*, 44(1), 48-62.
  - Robati, D., Mirza, B., Rajabi, M., Moradi, O., Tyagi, I., Agarwal, S., & Gupta, V. K. (2016). Removal of hazardous dyes-BR 12 and methyl orange using graphene oxide as an adsorbent from aqueous phase. *Chemical Engineering Journal*, 284, 687-697.
  - Romero-Pérez, A., García-García, E., Zavaleta-Mancera, A., Ramírez-Bribiesca, J. E., Revilla-Vázquez, A., Hernández-Calva, L. M., & Cruz-Monterrosa, R. G. (2010). Designing and evaluation of sodium selenite nanoparticles in vitro to improve selenium absorption in ruminants. *Veterinary research communications*, 34(1), 71-79.
  - Rangabhashiyam, S., Anu, N., Nandagopal, M. G., & Selvaraju, N. (2014). Relevance of isotherm models in biosorption of pollutants by agricultural byproducts. *Journal of Environmental Chemical Engineering*, 2(1), 398-414.
  - Rafeah, N. T., & Fadilah, S. A. (2009). The ABC of haematopoietic stem cell transplantation. *The Medical journal of Malaysia*, 64(1), 94-100.
  - Rook, F., Hadingham, S. A., Li, Y., & Bevan, M. W. (2006). Sugar and ABA response pathways and the control of gene expression. *Plant, cell & environment*, 29(3), 426-434.
  - Safri, S. N. A., Sultan, M. T. H., Jawaid, M., & Jayakrishna, K. (2018). Impact behaviour of hybrid composites for structural applications: A review. *Composites Part B: Engineering*, 133, 112-121.

- Sardella, F., Gimenez, M., Navas, C., Morandi, C., Deiana, C., & Sapag, K. (2015). Conversion of viticultural industry wastes into activated carbons for removal of lead and cadmium. *Journal of Environmental Chemical Engineering*, 3(1), 253-260.
- Sari, A., Tuzen, M., Citak, D., & Soylak, M. (2007). Equilibrium, kinetic and thermodynamic studies of adsorption of Pb (II) from aqueous solution onto Turkish kaolinite clay. *Journal of hazardous materials*, 149(2), 283-291.
- Sulyman, A. I., Alwarafy, A., MacCartney, G. R., Rappaport, T. S., & Alsanie, A. (2016). Directional radio propagation path loss models for millimeter-wave wireless networks in the 28-, 60-, and 73-GHz bands. *IEEE Transactions on Wireless Communications*, 15(10), 6939-6947.
- Satapathy, D., & Natarajan, G. S. (2006). Potassium bromate modification of the granular activated carbon and its effect on nickel adsorption. *Adsorption*, 12(2), 147-154.
- Satish, S., Mohana, D. C., Ranhavendra, M. P., & Raveesha, K. A. (2007). Antifungal activity of some plant extracts against important seed borne pathogens of *Aspergillus* sp. *Journal of Agricultural technology*, 3(1), 109-119.
- Savage, N., & Diallo, M. S. (2005). Nanomaterials and water purification: opportunities and challenges. *Journal of Nanoparticle research*, 7(4-5), 331-342.
- Savage, N., & Diallo, M. S. (2005). Nanomaterials and water purification: opportunities and challenges. *Journal of Nanoparticle research*, 7(4-5), 331-342.
- Selomulya, C., Meeyoo, V., & Amal, R. (1999). Mechanisms of Cr (VI) removal from water by various types of activated carbons. *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology*, 74(2), 111-122.
- Selvakumari, G., Murugesan, M., Pattabi, S., & Sathishkumar, M. (2002). Treatment of electroplating industry effluent using maize cob carbon. *Bulletin of environmental contamination and toxicology*, 69(2), 195-202.
- Shoukry, Y., El-Kharashi, M. W., Hammad, S., Kumar, A., & Bahig, G. (2015). Software Allocation in Automotive Networked Embedded Systems: A Graph-Based Approach. In *Languages, Design Methods, and Tools for Electronic System Design* (pp. 207-221). Springer, Cham.

- Selvi, K., Pattabhi, S., & Kadirvelu, K. (2001). Removal of Cr (VI) from aqueous solution by adsorption onto activated carbon. *Bioresource technology*, 80(1), 87-89.
- Sengupta, K., Banerjee, S., Saxena, N. K., & Banerjee, S. K. (2004). Thombospondin-1 Disrupts Estrogen-Induced Endothelial Cell Proliferation and Migration and Its Expression Is Suppressed by Estradiol11NIH/National Cancer Institute CA87680 (SK Banerjee), VA Merit Review grant (SK Banerjee), Midwest Biomedical Research Foundation grant and NIH COBRE award 1 P20 RR15563 (S. Banerjee), and matching support from the State of Kansas. *Molecular Cancer Research*, 2(3), 150-158.
- Shanthi, S., & Mahalakshmi, T. (2012). Studies on the removal of Malachite Green and Methylene Blue dyes from aqueous solutions of their binary mixture by adsorbtion over Commercial Activated Carbon and Tamarind Kernel Powder. *International Journal of Research in Pharmacy and Chemistry*, 2(2), 289-298.
- Sharma, D. C., & Forster, C. F. (1994). A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents. *Bioresource Technology*, 47(3), 257-264.
- Singh, A., & Kumari, P. (2018). Two-dimensional elasticity solution for arbitrarily supported axially functionally graded beams. *Journal of Solid Mechanics*, 10(4), 719-733.
- Sivakumar, D., & Nouri, J. (2015). Removal of contaminants in a paper mill effluent by *Azolla caroliniana*.
- Skalickova, S., Milosavljevic, V., Cihalova, K., Horky, P., Richtera, L., & Adam, V. (2017). Selenium nanoparticles as a nutritional supplement. *Nutrition*, 33, 83-90.
- Smith, S. C., & Rodrigues, D. F. (2015). Carbon-based nanomaterials for removal of chemical and biological contaminants from water: a review of mechanisms and applications. *Carbon*, 91, 122-143.
- Sultan, M., Miyazaki, T., & Koyama, S. (2018). Optimization of adsorption isotherm types for desiccant air-conditioning applications. *Renewable Energy*, 121, 441-450.
- Su, H., Ye, Z., & Hmidi, N. (2017). High-performance iron oxide-graphene oxide nanocomposite adsorbents for arsenic removal. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 522, 161-172.
- Theron, J., Walker, J. A., & Cloete, T. E. (2008). Nanotechnology and water treatment: applications and emerging opportunities. *Critical reviews in microbiology*, 34(1), 43-69.

- Thitame, P. V., & Shukla, S. R. (2017). Removal of lead (II) from synthetic solution and industry wastewater using almond shell activated carbon. *Environmental Progress & Sustainable Energy*, 36(6), 1628-1633.
- Tay, T., Ucar, S., & Karagöz, S. (2009). Preparation and characterization of activated carbon from waste biomass. *Journal of Hazardous Materials*, 165(1-3), 481-485.
- Taffarel, S. R., & Rubio, J. (2009). On the removal of Mn<sup>2+</sup> ions by adsorption onto natural and activated Chilean zeolites. *Minerals Engineering*, 22(4), 336-343.
- Valerio, M. E., García, J. F., & Peinado, F. M. (2007). Determination of phytotoxicity of soluble elements in soils, based on a bioassay with lettuce (*Lactuca sativa* L.). *Science of the Total Environment*, 378(1-2), 63-66.
- Vieira, R. H., & Volesky, B. (2000). Biosorption: a solution to pollution. *International microbiology*, 3(1), 17-24.
- Villaescusa, I., Fiol, N., Martínez, M., Miralles, N., Poch, J., & Serarols, J. (2004). Removal of copper and nickel ions from aqueous solutions by grape stalks wastes. *Water research*, 38(4), 992-1002.
- Vunain, E., Mishra, A. K., & Mamba, B. B. (2016). Dendrimers, mesoporous silicas and chitosan-based nanosorbents for the removal of heavy-metal ions: a review. *International journal of biological macromolecules*, 86, 570-586.
- Wang, Y., & Herron, N. (1991). Nanometer-sized semiconductor clusters: materials synthesis, quantum size effects, and photophysical properties. *The Journal of Physical Chemistry*, 95(2), 525-532.
- Wong, W. H., Levinton, J. S., Twining, B. S., Fisher, N. S., Kelaher, B. P., & Alt, A. K. (2003). Assimilation of carbon from a rotifer by the mussels *Mytilus edulis* and *Perna viridis*: a potential food-web link. *Marine Ecology Progress Series*, 253, 175-182.
- Wu, H., D'Alessio, A. C., Ito, S., Wang, Z., Cui, K., Zhao, K., & Zhang, Y. (2011). Genome-wide analysis of 5-hydroxymethylcytosine distribution reveals its dual function in transcriptional regulation in mouse embryonic stem cells. *Genes & development*, 25(7), 679-684.

- Xue, Z., Wang, S., Lin, L., Chen, L., Liu, M., Feng, L., & Jiang, L. (2011). A novel superhydrophilic and underwater superoleophobic hydrogel-coated mesh for oil/water separation. *Advanced Materials*, 23(37), 4270-4273.
- Yao, Y., Shankar, R., Kats, M. A., Song, Y., Kong, J., Loncar, M., & Capasso, F. (2014). Electrically tunable metasurface perfect absorbers for ultrathin mid-infrared optical modulators. *Nano letters*, 14(11), 6526-6532.
- Zhang, F., Pant, D., & Logan, B. E. (2011). Long-term performance of activated carbon air cathodes with different diffusion layer porosities in microbial fuel cells. *Biosensors and Bioelectronics*, 30(1), 49-55.
- Zhao, Y. G., Shen, H. Y., Pan, S. D., & Hu, M. Q. (2010). Synthesis, characterization and properties of ethylenediamine-functionalized Fe<sub>3</sub>O<sub>4</sub> magnetic polymers for removal of Cr (VI) in wastewater. *Journal of Hazardous Materials*, 182(1-3), 295-302.
- Zhuang, J., Liu, Y., Wu, Z., Sun, Y., & Lin, L. (2009). Hydrolysis of wheat straw hemicellulose and detoxification of the hydrolysate for xylitol production. *BioResources*, 4(2), 674-686.
- Zornoza, B., Martinez-Joaristi, A., Serra-Crespo, P., Tellez, C., Coronas, J., Gascon, J., & Kapteijn, F. (2011). Functionalized flexible MOFs as fillers in mixed matrix membranes for highly selective separation of CO<sub>2</sub> from CH<sub>4</sub> at elevated pressures. *Chemical communications*, 47(33), 9522-9524.
- Zwiener, C., Richardson, S. D., De Marini, D. M., Grummt, T., Glauner, T., & Frimmel, F. H. (2007). Drowning in disinfection byproducts? Assessing swimming pool water. *Environmental Science & Technology*, 41(2), 363-372.

## APPENDIX

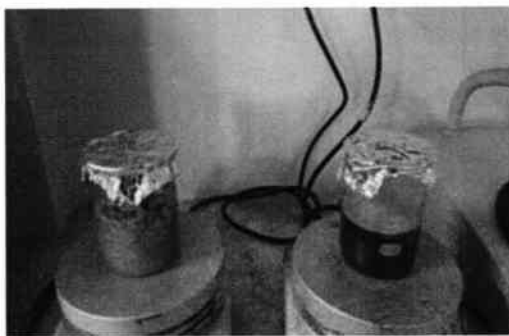
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**Collection of Sample**



**Washing and Drying of Sample**



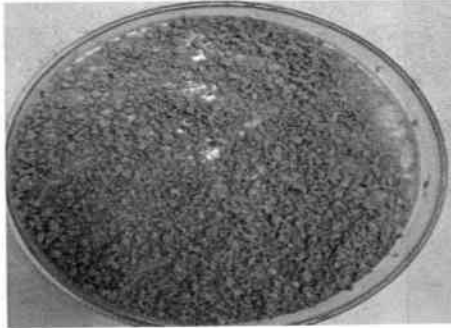
**Heating of sample mixed with  
NaOH**



**Washing with Distilled water**

## APPENDIX

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**Activated OP**



**Addition of NPs with OP**



**Heating of OP with NP**



**pH Meter**



**Muffle Furnace**



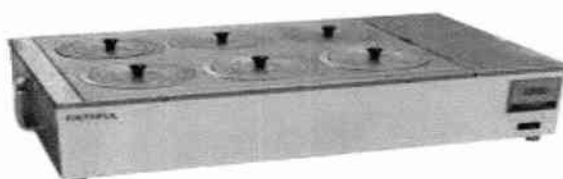
**Vibrator**

## APPENDIX

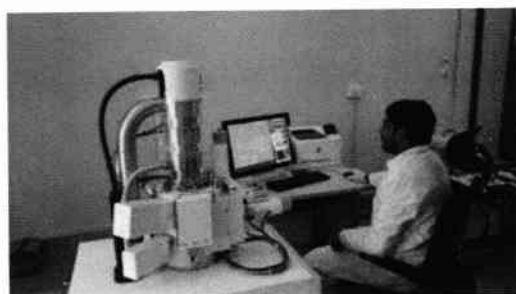
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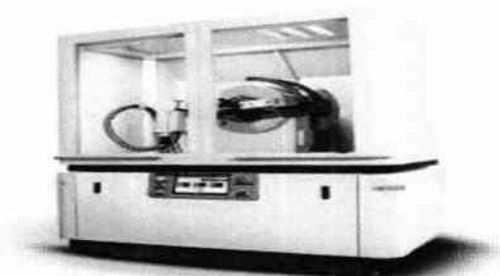
Hot plate



Water bath



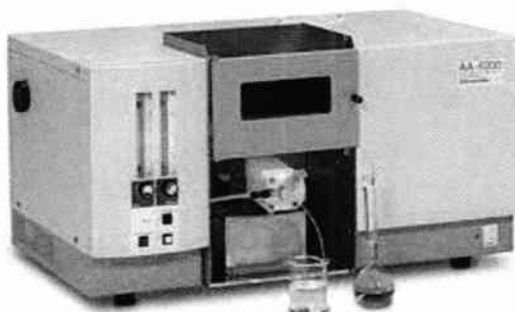
SEM



XRD



FT-IR



AAS