UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF GRAPE SEEDS BIOCHAR AND IRON NANOPARTICLES-ADDED BIOCHAR FOR REMOVAL OF CADMIUM FROM AQUEOUS SOLUTIONS

AL ERCHELEE ALAA JASSEM MOHAMMED

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By

AL ERCHELEE ALAA JASSEM MOHAMMED

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

November 2021

DEDICATION

This thesis is dedicated toMy lovely parents:

With love, respect, and a bunch of memories

Indeed, we belong to Allah, and indeed to him, we will return.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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November 2021

Chairman : Syaizwan Zahmir Zulkifli, PhD
Faculty : Science

Due to the degradation of environmental quality, particularly in relation to the rising heavy metal concentrations in the environment, methods for removing these contaminants have been widely studied this study aims to investigate the adsorption method for cadmium removal in an aqueous solution using biomass-derived adsorbents. Grape seeds (GS) were used as biomass precursors to prepare grape seeds biochar (GSB) and to synthesize grape seeds-iron nanoparticles (GS-IONPs) for the purpose of removing cadmium ion (Cd) from aqueous solutions using batch adsorption technique. The GSB was prepared at a percentage yield of 48-50% by carbonization of dry grape seeds particles (0.5 mm) at 400 ^{o}C under inert gas (N_2). The grape seeds iron oxide nanoparticles were prepared by bio-reduction of ferrous chloride salt, using grape seeds water extract. The opt optimum operating conditions of biosynthesis nanoparticles consist of mixing ferric chloride with grape seed water extract in a 2:1 v/v ratio and solution mixture with pH of 3.8. The feasibility of adsorbents to remove Cd from aqueous solutions was investigated through batch studies using the GSB and GS-IONPs, in addition to the commercial charcoal (CC) as adsorbents. Batch experiments were carriedout to study the effects of cadmium initial concentrations in the range of 10-25 mg/l, contact time and solution pH (2-12) at solution temperature (30 ^{o}C). Batch adsorption ofCd onto the three adsorbents was fitted to the Langmuir, Freundlich, and Temkin isotherm models. It was found that the adsorption of cadmium onto GSB, GS-IONPs andCC followed the Langmuir isotherm model according to the R^2 values ($0.999 \geq R^2 \geq 0.970$), in addition to the 1/n values, which are less than one. The maximum adsorption capacities were found to be 10.63, 16.3 and 11.12 mg/g onto GSB, GS-IONPs and CC, respectively. Please add a conclusion here.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SINTESIS DAN CIRI BIOCHAR BIOCHAR BIJI ANGGUR DAN ZARAH NANO BESI-TAMBAH BIOCHAR UNTUK PENYELESAIAN KADMIUM DARIPADA PENYELESAIAN AIR

Oleh

AL ERCHELEE ALAA JASSEM MOHAMMED

November 2021

Pengerusi : Syaizwan Zahmir Zulkifli, PhD
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Disebabkan kemerosotan kualiti alam sekitar, terutamanya di kawasan bandar, telah meningkat, yang menunjukkan bahawa kepekatan logam berat di atmosfera semakin meningkat, dan kesan kesihatan logam berat dalam tanaman makanan tercemar yang diairi dengan air sisa mendapati pengumpulan berat yang besar. logam dalam tanah pengairan air sisa yang dikumpul dari pelbagai bahagian di Malaysia dan dunia. Biji anggur (GS) digunakan sebagai prekursor biojisim untuk menyediakan biochar biji anggur (GSB) dan untuk mensintesis biji anggur-zarah besi besi (GS-IONPs) untuk penyingkiran ion kadmium (Cd) daripada larutan akueus menggunakan teknik penjerapan kelompok. Biochar biji anggur (GSB) disediakan pada peratusan hasil 48-50% dengan pengkarbonan zarah biji anggur kering (0.5 mm) pada 400 ^{o} C di bawah gas lengai (N_2). Nanopartikel besi oksida biji anggur (GS-IONPs) disediakan melalui pengurangan bio garam ferus klorida, menggunakan ekstrak air biji anggur. Keadaan operasi optimum nanopartikel biosintesis terdiri daripada mencampurkan ferik klorida dengan ekstrak air biji anggur dalam nisbah 2:1 v/v dan campuran larutan pH= 3.8. Kebolehlaksanaan penjerap untuk mengeluarkan (Cd) daripada larutan akueus telah disiasat melalui kajian kelompok menggunakan (GSB dan GS-IONPs) sebagai tambahan kepada arang komersial (CC) sebagai penjerap. Eksperimen kelompok telah dijalankan untuk mengkaji kesan kepekatan kadmium awal dalam julat 10-25 mg/l, masa sentuhan, dan pH larutan (2-12) pada suhu larutan (30 ^{o} C). Penjerapan kelompok kadmium pada penjerap telah dipasang pada model isoterma Langmuir, Freundlich, dan Temkin, didapati bahawa penjerapan kadmium pada GSC, GS-IONP dan CC mengikut model isoterma Langmuir mengikut nilai R2 ($0.999 \geq R2 \geq 0.970$) sebagai tambahan kepada nilai 1/n, yang kurang daripada satu. Kapasiti penjerapan maksimum didapati 10.63, 16.3, dan 11.12 mg/g pada GSB, GS-IONP dan CC, masing-masing.

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This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

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LIST OF ABBREVIATIONS

FAO	Food and agriculture organization
nm	Nanometre
EPA	American Environmental Protection Agency
WHO	World Health Organization
$FeCl_2$	Ferrous chloride
GS	Grape Seed
GSB	Grape Seed Biochar
GS-IONPs	Grape Seed-Iron Oxide Nanoparticles CC Commercial Charcoal
Cd	Cadmium
UF	Ultrafiltration
ED	Electro dialysis
MIONPs	Magnetic iron oxide nanoparticles
BET	Brunauer-Emmett-Teller
SEM	Scanning Electron Microscopy
FTIR	Fourier-transform infrared spectroscopy
rpm	Revolutions per minute
A_i	Absorbance
ε	Molar absorptivity coefficient
Λ	Wavelength
b_c	Cell path length
C	Solute concentration
Co	Initial solute concentration

Ce	Solute concentration at equilibrium
Ct	Solute concentration at time
R^2	Corelation coefficient
Q	Adsorption capacity
q_e	Adsorption capacity at equilibrium
q_t	Adsorption capacity at time
q_m	Maximum adsorption capacity
TGA	Thermogravimetric analysis
XRD	X-ray diffractometers
µm	Micrometres
g	Gram
mm	Millimetre

CHAPTER 1

INTRODUCTION

1.1 Introduction

This chapter provides an overview of the thesis background. Existing heavy metal situations identified in water, soil, and air are included in the spectrum. There is a growing need to discover a more dependable and cost-effective solution to deal with the daily dumping of dangerous compounds into the atmosphere, such as heavy metals. To cleanse wastewater, heavy metals can be removed using a number of ways, including adsorption onto carbons and nano adsorbents. In this chapter, the issue definition and analysis goals, as well as the research organization, are described.

1.2 Water Contamination

In the global climate, water pollution is a big issue, and it is considered a growing 21st century problem all over the world. Due to water pollution, quality water becomes gradually deteriorated. This can threaten aquatic life and its biodiversity, which is the most distinctive feature of life. There are many reasons for water pollution that may affect aquatic biodiversity (Bassem, 2020).

If river water is not contaminated by human activities, it is generally potable (fit for human consumption) with minimal care. Rivers, on the other hand, are also being used to dispose of liquid and solid waste in several countries. If the government must fix river contamination issues, as it is doing, end-user understanding and participation are critical for such a critical aspect of water management. When small or large amounts of materials (pollutants) are added to water, it causes a body of water to become contaminated. The main sources of water contamination are listed in Figure 1. 1 (Afroz et al., 2014).

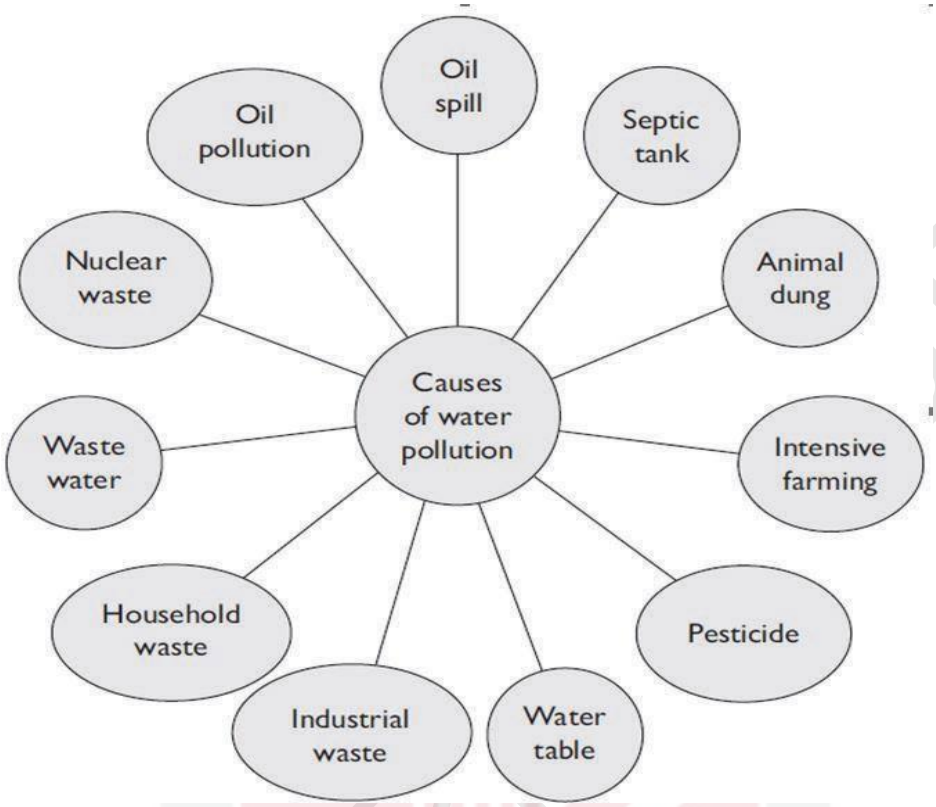

Figure 1.1 : The main sources of water pollution (Afroz et al., 2014)

Surface and groundwater are sources of water that have often been polluted. Agriculture makes extensive use of this type of water. According to a survey, more than 50 nations with a combined area of 20 million hectares utilize dirty or partially treated water (Ashraf, 2012). Polluted water can be reutilized to offset the effects of water in a variety of ways. Any water contamination effects are obvious right away, although others take months or years to manifest. Toxins are recycled from polluted water to livestock and then to humans by the intake of food such as meats and dairy, allowing chemicals to join the food chain. Drinking polluted water can cause infectious diseases such as typhoid and cholera. which is associated with microbial water contamination. If dirty water is consumed on a daily basis, it can impact the human heart and kidneys. Poor blood supply, skin infections, vomiting, and nervous system disruption are some of the other health issues linked to polluted water. Indeed, water contamination is thought to be the leading cause of mortality for humans all over the world. Every year, more than 2 million children under the age of five die in the third world as a result of consuming contaminated water. Healthy life is something that everyone in human society desires for themselves, their children, and for the broader economic and social benefits it provides. It is extremely important for long-term economic growth and sustainability (Ghafoor et al., 1994).

1.3 Heavy Metals

A growing concern of the environmental issue is related to the presence of heavy metals is the presence of heavy metals and other harmful aromatic hydrocarbons and trace elements in our environment. Notably, harmful health effects are generally associated with some transition of metals (Ashraf, 2012).

From another perspective, lead and cadmium, as for instance, have long half-lives (10 to 12 years), after exposure to smoke in tissues and fluids. Biomonitoring tests indicate that cigarettes have levels of lead and cadmium considerably greater than non-smokers. In non-smokers who are chronically exposed to secondhand smoke, bioaccumulation of metals has also been shown (Lamarque et al., 2012). Smoking-related diseases can be attributed to the inhalation of many different toxins including the heavy metal. Heavy metals like lead have been shown to affect various biochemical processes in the human body including calcium metabolism and the activation of cell death pathways, which are involved in carcinogenesis (Siddoo-Atwal, 2017).

When they are not metabolized by the body, heavy metals become toxic and accumulate in the liver, bone, hair, and soft tissue. When they are exposed to humans in agriculture, manufacturing, medicinal, industrial or residential conditions, they may reach the human body through food, water, air or absorption through the skin. Industrial exposure is a popular route for a single exposure (Herawati et al., 2000). The main sources of heavy metals are shown in Figure 1. 2 (Kumar et al., 2016).

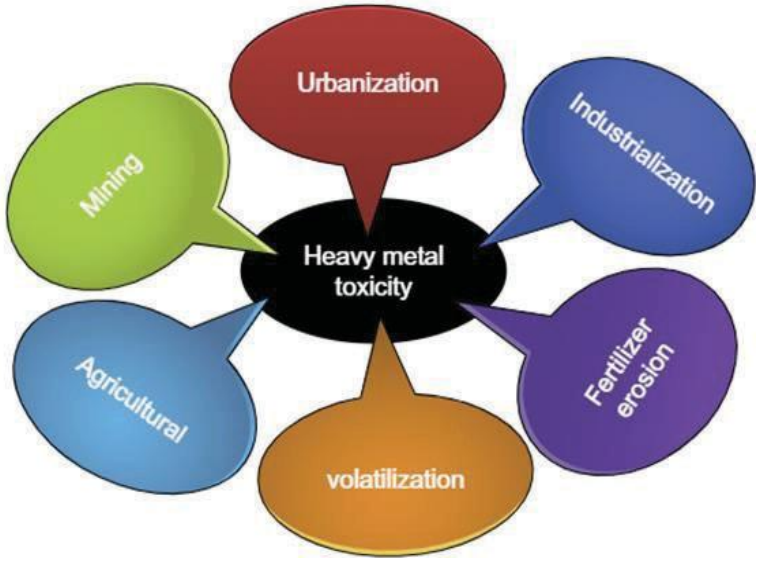

Figure 1.2 : Sources of metal ions (adapted from Kumar et al., 2016)

1.4 Problem Statement

The rapid industrialization in Malaysia coupled with global concern about environmental issues has fueled environmental consciousness in the region. In recent years, studies on the degradation of environmental quality, particularly in urban areas, have increased. Previous studies have shown that study into the health effects of heavy metals in polluted food crops irrigated with wastewater found a substantial build-up of heavy metals in wastewater-irrigated soils collected from different parts of Malaysia. The anthropogenic contribution of heavy metals into the coastal ecosystem of Malaysia suggests that, there are compelling reasons to presume increasing quantities of heavy metals in the coastal sediments (Mustapha, 2013). The consequence is the rise in the background amount of all the toxins along the waterways. It was also found that the amount of pollution in the river during the rainy season is comparatively lower as compared to the dry season. Recently, great development around Malaysia, especially Peninsular Malaysia such as industrialization, urbanization, the advancement of agriculture and other activities related to the modern era are occurring rapidly, which have directly influenced the coastal ecosystems that contain aquatic resources (Kamaruzzaman and Ong, 2009). Department of Environment, Ministry of Natural Resources and Environment Malaysia stated in every annual report the activities that can be the sources of anthropogenic pollutants and potentially contaminate the coastal environment. Until recently, there have been a number of reports on the status of trace elements in the aquatic environment in Malaysia (Zulkifli et al., 2010). Nevertheless, continuous long-term monitoring is needed to assess the toxic heavy metals in rivers, as it could have effects on food chains, which are ultimately consumed by humans (Hossen et al., 2015). Heavy metals have been removed using a variety of methods, either alone or in conjunction with others. Because of its low cost, availability, and environmental friendliness. adsorption process is widely used to remove heavy metals from wastewater with high removal capacity (Mulana et al., 2018). Adsorption is the most widely used technology for purifying water that has been contaminated with heavy metals and other hazardous chemicals. So far, adsorption was found to be a superior technique for the removal of metal ions from aqueous solutions, in terms of cost, wide range of applications, simplicity of design, the availability of a wide range of adsorbents, a small amount of by-products, reusable adsorbents, and high efficiency (Lakherwal. 2014). The applicability of nanoparticles as adsorbent materials in solving environmental problems has been widely studied in recent years due to unique physicalysical and chemical properties that make them superior to traditional sorbents (Mahmud et al., 2016). The ability in terms of functionalization, of some specific functional groups on their surface, allows the synthesis of various types of nanoparticles being used to remove contaminants: organic and inorganic (Faghihi et al., 2016). Even though waste water treatment is extensively studied, efficient technology with high capacity to remove toxic pollutants from the environment are still needed (Ianoş et al., 2014). In this study two types of adsorbents were prepared: grab seeds biochar (GSB) and grape seeds iron oxide nano particles adsorbent (GS-ionps) for the purpose of removing cadmium ion (Cd) from synthetic wastewater.

1.5 Objectives of the study

The followings are the objectives of the study carried out:

1) Prepare new types of adsorbents, i.e. grape seeds biochar and grape seeds iron oxide nanoparticles.
2) Characterize the prepared grab seeds biochar (GSB) and grape seeds iron oxide nanoparticles (GS-IONPs) for their chemical and physical properties.
3) Investigate the effects of cadmium (Cd) initial concentrations, contact time, and solution pH on the removal of Cd onto adsorbents (GSB and GS-IONPs) and commercial charcoal in a batch adsoprtion process.
4) Evaluate the adsorption behavior of Cd onto the adsorbents using Langmuir, Freundlich, and Temkin isotherm models.

1.6 Thesis Structure

The thesis consists of five chapters, including, plus appendices that detail the work accomplished. A overview of water contaminants and heavy metals in water is presented in Chapter 1 (Introduction), as well as how these heavy metals may be removed by adsorption utilizing biochar and nanoparticles as adsorbents. In Chapter 2, heavy metal removal, adsorption, biochar, and nanoparticle adsorbents, as well as their preparation methods, were comprehensively examined. This includes a review of adsorbent characterization and adsorption isotherm evaluation. Chapter 3 (methodolgy) provides details of materials and instruments used, as well as laboratory procedures such as the preparation of adsorbent and nanoparticles, experimental settings and data analysis. While chapter 4 describes the data obtained and discusses the results, chapter 5 summarizes the findings and provides recommendation for future research.

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APPENDICES

Appendix A : Cadmium Calibration Curve

Table A1 : Cadmium calibration values

Concentrations (mg/l)	Absorbance
0	*0*
5	*0.065*
10	*0.130*
15	*0.195*
20	*0.260*
25	*0.325*
30	*0.390*

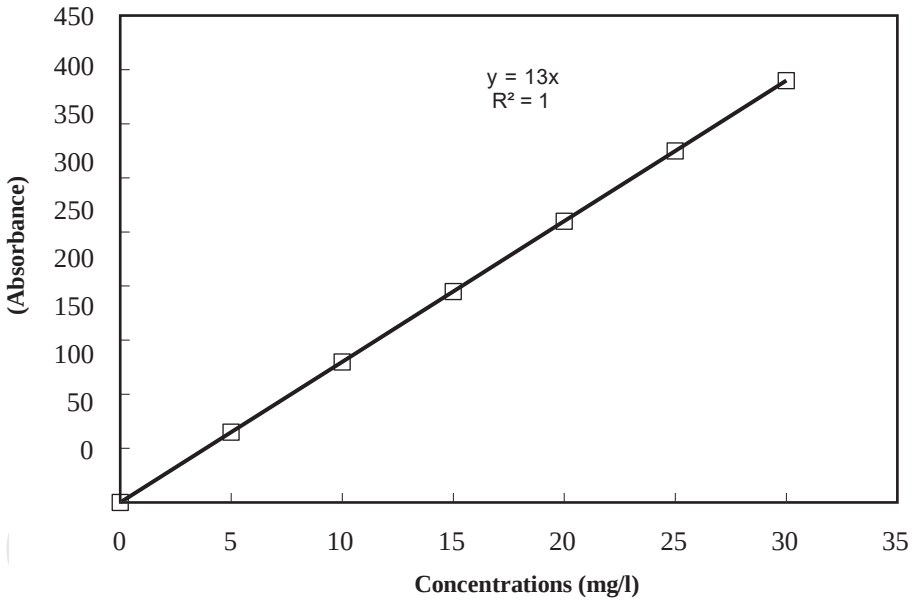

Figure A1 : Cadmium calibration curve

Appendix B : The adsorption capacity and concertation curves for cadmium at equilibrium using GSB, GS-IONPs and CB shown in Figures (4. 2, 4.3 and 4.4)

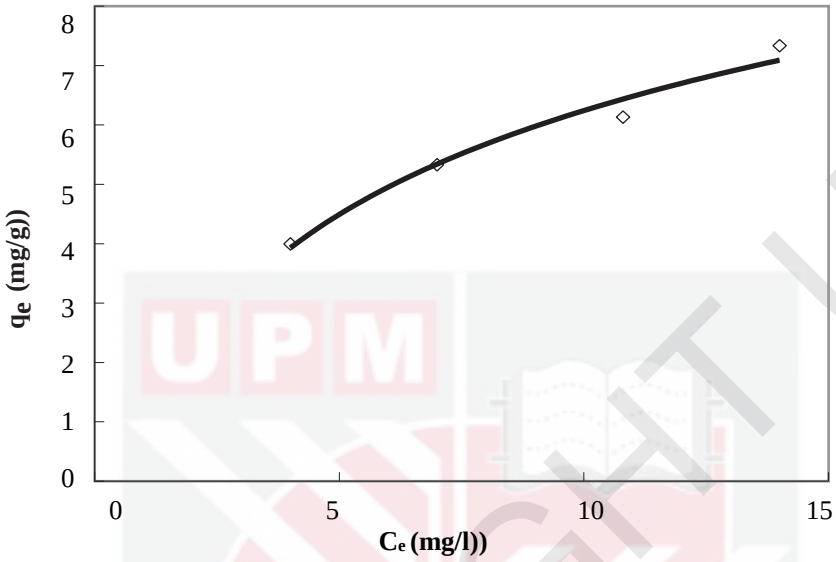

Figure B2 : Cadmium adsorption vs concertation at equilibrium using GSB as Adsorbent at 30 ^{o}C

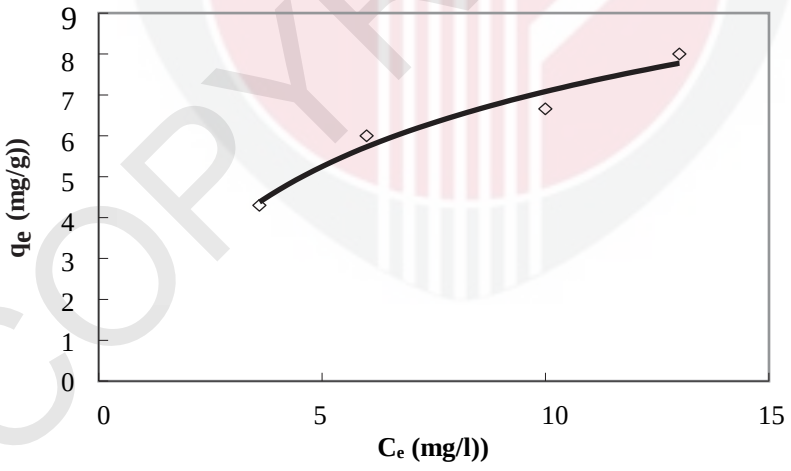

Figure B3 : Cadmium adsorption vs concertation at equilibrium using CC as adsorbent at 30 ^{o}C

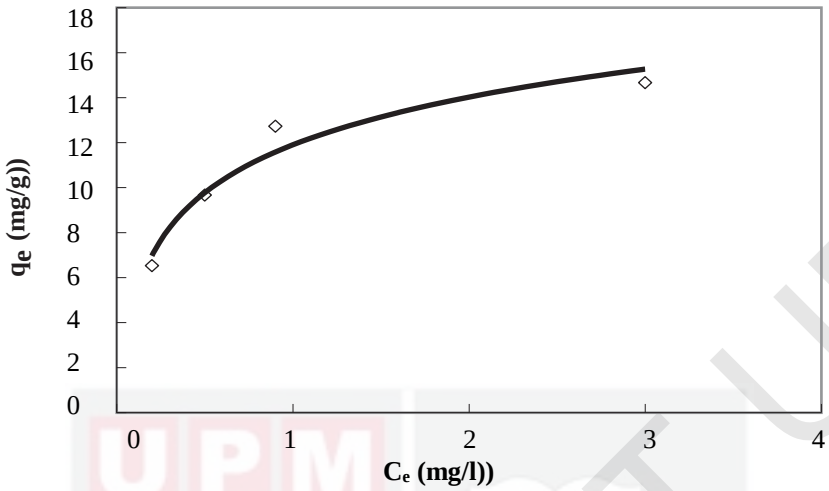

Figure B4 : Cadmium adsorption vs concertation at equilibrium using GS-IONPs as adsorbent at 30 ºC

BIODATA OF STUDENT

Al Erchelee Alaa Jassem Mohammed, was born in 1993, Baghdad, Iraq. She got her BSc in science biology from Madinit Alilm university college, Iraq in 2017. She worked as laboratories staff members in Green Barrows Company for environmental services until the end of 2018, she was attended her MSc study in biology department, Faculty of science, University Putra Malaysia (UPM) and completed it in 2020. She got acceptance letter for her PhD study in the same university (UPM) and will start her program on September 2022. She published some of the manuscripts in scientific journals and she participated many scientific conferences, meeting and workshop.

LIST OF PUBLICATIONS

Published papers in ISI-indexed journals

Alaa Jasim Mohammed, Mohd Hafiz Ibrahim, Syaizwan Zahmir Zulkifli and Jasim Mohammed Salman (2021). Synthesis and Characterization of Nano- adsorbent Derivative Derived from Grape Seeds for Cadmium Ion Removal from Aqueous Solution. Water 2021, 13, (1-12). https://doi.org/10.3390.

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1. Alaa Jasim Mohammed, and Jasim M. Salman (2021). The 1st international scientific conference for the scientific association of Iraqi academics and intellectuis, Iraq, Baghdad, December 2021.

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