

Utilization of Some Solid Wastes in the Field of Water Treatment

A Thesis

Submitted for Ph.D Degree in Chemistry

By
Sayed Ahmed Othman Abo El-Dahab
M.Sc. Chemistry, (2008)

Supervised by

Prof. Dr. Salah A. Abo-El-Enein (D.Sc.)

Professor of Physical Chemistry& Building Materials, Faculty of Science, Ain Shams University

Prof. Dr. Fayza Sayed Mohamed Hashem

Professor of Physical Chemistry, Faculty of Science, Ain Shams University

Dr. Safaa Mohamed Awwad El-Gamal

Associated Professor of Physical Chemistry, Faculty of Science, Ain Shams University



Ain Shams University Faculty of Science Chemistry Department

Utilization of Some Solid Wastes in the Field of Water Treatment

A Thesis

Submitted for Ph.D Degree in Chemistry

Ву

Sayed Ahmed Othman Abo El-Dahab M.Sc. Chemistry, (2008)

Supervised by

Prof. Dr. Salah A. Abo-El-Enein (D.Sc.) -----

Professor of Physical Chemistry& Building Materials, Faculty of Science, Ain Shams University

Prof. Dr. Fayza Sayed Mohamed Hashem

Dr. Safaa Mohamed Awwad El-Gamal -----

Associated Professor of Physical Chemistry, Faculty of Science, Ain Shams University

Head of Chemistry Department

Prof. Dr. Ibrahim H. A. Badr

Cairo - 2018



Ain Shams University Faculty of Science Chemistry Department

Utilization of Some Solid Wastes in the Field of Water Treatment

A Thesis

Submitted for Ph.D. Degree in Chemistry
By

Sayed Ahmed Othman Abo-El-Dahab M.Sc. Chemistry, (2008)

Approved by

Faculty of Science, Ain Shams University

Prof. Dr. Mahmoud Ahmed Mohamed Mousa -----

Professor of Physical Chemistry & Materials Science, Faculty of Science, Benha University

Prof. Dr. Ashraf Abd-El-Aziz El-Bendary -----

Professor of Inorganic & Analytical Chemistry, Faculty of Science, Damietta University

Head of Chemistry Department

Prof. Dr. Ibrahim H. A. Badr Cairo – 2018



ACKNOWLEDGEMENT

First and foremost, I would like to thank Allah for giving me the opportunity and the strength to accomplish this work.

I would like to express my deep gratitude to **Prof. Dr. Salah A. Abo-El-Enein (D.Sc.)** Professor of Physical Chemistry & Building Materials, Faculty of Science, Ain Shams University.

I would like to express my deep gratitude to **Prof. Dr. Fayza Sayed Mohamed Hashem** Professor of physical chemistry, Faculty of Science, Ain Shams University, for her valuable supervision, advice, unlimited support and constructive suggestions throughout the thesis.

I would like to express my deep gratitude to **Dr. Safaa**Mohamed Awwad El-Gamal Associated Prof. of physical chemistry, Faculty of Science, Ain Shams University, for her valuable supervision, advice, unlimited support and constructive suggestions throughout the thesis.

I owe great thanks and sincere love to my wife for her encouragement and support throughout my work.

Sayed Ahmed Othman Abo El-Dahab

List of Abbreviation

Symbol	Description
WHO	World health organization
TDS	Total dissolved salts
TSS	Total suspended solids
WTS	Water treatment sludge
PCB	Powder calcined brick
WBD	Waste brick dust
COD	Chemical oxygen demand
SMWW	Standard methods for the examination of
SIVIVV	water and wastewater
FA	Fly ash
DWTS	Drinking water treatment sludge
LWBW	Light white brick waste
HOMRA	Red brick waste
ICP	Inductive coupled plasma
XRD	X-ray diffraction
XRF	X-ray florescence
EDX	Energy Dispersive X-ray
SEM	Scanning electron microscope
CSH	Calcium silicate hydrates
CS	Calcium silicate

ELSEVIER

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay



Research paper

Drinking water treatment sludge as an efficient adsorbent for heavy metals removal



S.A. Abo-El-Enein^a, Ahmed Shebl^a,*, S.A. Abo El-Dahab^b

- ^a Chemistry Department, Faculty of Science, Ain Shams University, Abbassia 11566, Cairo, Egypt
- ^b Holding Company for Water and Wastewater, Egypt

ARTICLE INFO

Keywords: Drinking water treatment sludge Lead cadmium nickel removals Adsorption Quartz Illite Albite

ABSTRACT

Green chemists paid much more attention towards the alternative ways to reutilize waste materials instead of its disposal in a non-ecofriendly manner. In this study, drinking-water treatment sludge (DWTS), which is a byproduct resulted from drinking water treatment plants, was successfully applied as an adsorbent for Pb(II), Cd(II) and Ni(II) removal from wastewater. The physicochemical characteristics of DWTS were investigated using X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM) and $\rm N_2$ adsorption-desorption isotherms

The XRD analysis revealed that the DWTS under study consists of quartz and illite phases which had been reported for their adsorption efficiency. Firing of DWTS at $500\,^{\circ}\text{C}$ causes the appearance of albite phase in addition to previous ones which enhances the adsorption capacity of these materials. The influence of different parameters such as firing temperature of DWTS, contact time, pH, DWTS dose and initial metal ions concentration on the adsorption of heavy metal ions and, consequently, on their removal were investigated. DWTS exhibit an adsorption efficiency towards Pb(II) > Cd(II) > Ni(II). The extremely high efficiency of DWTS towards Pb(II) adsorption can nominate it as a specific low-cost adsorbent for Pb ions.

1. Introduction

Drinking-water treatment sludge (DWTS) is a by-product from the coagulation-flocculation process using aluminum or iron based salts to precipitate clay, colloidal particles, algae and humic substances from water resources. Due to its high production rate and its environmentally unfavored disposal to landfill, several researchers paid a considerable attention for using this waste material in different applications especially those of low cost. The chemical composition of DWTS varies depending on the source of water under treatment as well as the type of coagulant used. These applications include utilization of DWTS for ceramic products (Zamora et al., 2008; Kizinievic et al., 2013; Mymrin et al., 2017), cement and concrete production (Rodríguez et al., 2010; Sales et al., 2011; Hwang et al., 2017) as well as wastewater treatment as an adsorbent for the removal of phenolic compounds (Fragoso and Duarte, 2012), phosphates (Razali et al., 2007; Piaskowski, 2013), dyes from textile industry discharge (Chu, 1999) and heavy metals (Ippolito et al., 2011; Siswoyo et al., 2014).

Pollution of water resources by heavy metals such as lead, cadmium and nickel which are continuously discharged in huge amounts from different growing industrial activities has been recognized (Ribeiro The aim of this study is to get a beneficial use of DWTS as a low cost adsorbent for the removal of lead, cadmium and nickel metal ions from wastewater.

2. Experimental

2.1. Starting materials

The material used in this investigation is DWTS waste produced during 4 months from El-Fustat drinking water treatment plant (Egypt).

E-mail address: a_ahmed@sci.asu.edu.eg (A. Shebl).

et al., 2012; Yang and Cui, 2013; Keränen et al., 2015). These heavy metals are considered as hazardous materials where their toxicity to living organisms comes from their tendency to accumulate in living tissues since they are not biodegradable causing several health hazards like kidney problems, anemia, lung cancer and dyspnoea (Ahmaruzzaman, 2011; Visa et al., 2012). Therefore, a tremendous number of researches deals with the removal of such heavy metals especially via adsorption process (Bailey et al., 1999; Babel and Kurniawan, 2003; Ngah and Hanafiah, 2008; Tofighy and Mohammadi, 2015; Castaldi et al., 2015; Isaac et al., 2015; Dobrowolski et al., 2017; Azimi et al., 2017).

^{*} Corresponding author.

ABSTRACT

The objective of this study is to investigate the efficiency of using drinking water treatment sludge (DWTS), light white brick (LWBW) and red brick (HOMRA) wastes as solid adsorbents for the removal of heavy metal ions like lead, cadmium and nickel from their aqueous solution. The physicochemical characteristics of each solid waste were investigated using X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM) and N₂ adsorption-desorption isotherms. Besides, the effect of different parameters such as contact time, initial pH, initial metal ion concentrations, adsorbent dose and competition of metal ions on the adsorption of heavy metal ions was studied by using batch experiments. In addition, the effect of firing temperatures on the removal efficiency of these heavy metal ions from their solutions was investigated in case of DWTS. The removal efficiency at optimum conditions was approximately 100% for Pb⁺², Cd⁺² and Ni⁺² using DWTS and LWBW and 100, 20 and 9.7%, respectively using HOMRA. The adsorption kinetics of ions was followed the pseudo-second-order model based on the amounts of metal sorbed at various time intervals.

<u>Keywords:</u> Solid waste, heavy metals, wastewater, sludge, brick waste, low cost adsorbent.

List of Contents

Title	Page
List of figures	i
List of tables	V
Chapter I: Introduction and object of investigation	
IA. Introduction	1
IA.1. Sources of Drinking Water	2
IA.2. Contamination of Drinking Water Sources	3
IA.3. Pollution of Drinking Water Sources with	4
Heavy Metal Ions	4
IA.3.1. Lead metal	6
IA.3.2. Cadmium metal	7
IA.3.3. Nickel metal	8
IA.4. Different Methods of Heavy Metal Ions	9
Removal	7
IA.4.1. Heavy metal ions removal by chemical method	10
IA.4.2. Heavy metal ions removal by adsorption method	12
IA.4.2.1 Heavy metal ions removal by	12
silicate minerals	13
IA.4.2.2. Heavy metal ions removal by	22
sludge	
IA.4.2.3. Heavy metal ions removal by brick waste	26
IA.4.2.4. Heavy metal ions removal by other	31
solid wastes	40
IB. Object of Investigation	42
Chapter II: Materials and Methods of Investigation	
IIA. Starting Materials	44
IIA.1. Solid waste materials	44
IIA.2. Chemicals	45

Title	Page
IIB. Methods of Investigation	47
IIB.1. Adsorption Experiments	47
IIB.1.1. Effect of firing temperature	47
IIB.1.2. Effect of contact time	47
IIB.1.3. Effect of pH	48
IIB.1.4. Effect of adsorbent mass	48
IIB.1.5. Effect of initial heavy metal ions	70
concentration	49
IIB.1.6. Effect of competitive metal ions	49
IIB.2. Methods of Physicochemical Measurement	49
IIB.2.1. X-ray diffraction (XRD) analysis	50
IIB.2.2. X-ray florescence (XRF) analysis	50
IIB.2.3. Textural properties	50
IIB.2.4. Scanning electron microscope (SEM)	51
IIB.2.5. Inductive coupled plasma (ICP) analysis	51
IIB.2.6. Hydrogen ion concentration pH	52
Chapter III: Results and discussion	
IIIA. Removal Efficiency of Heavy Metal ions in Waste Water by Drinking Water Treatment Sludge (DWTS)	53
IIIA.1. Characterization of Drinking Water	
Treatment Sludge (DWTS)	53
IIIA.1.1. X-ray diffraction analysis	53
IIIA.1.2. Surface area and pore structure	56
characteristics of DWTS	56
IIIA.1.3. Morphology and microstructures of DWTS	63
IIIA.2. Factors Affecting the Removal Capacity	67
IIIA.2.1. Effect of firing temperature	67
IIIA.2.2. Effect of contact time	69
IIIA.2.3. Effect of initial solution pH	72

Title	Page
IIIA.2.4. Effect of DWTS adsorbent mass	75
IIIA.2.5. Effect of initial heavy metal ions	77
concentration	77
IIIA.2.6. Competitive heavy metal ions adsorption	79
IIIA.3. Kinetic Models	81
IIIA.3.1. The Pseudo-first-order model	81
IIIA.3.2. The pseudo-second-order model	85
IIIA.3.3. The intra-particle diffusion model	87
IIIA.4. Adsorption Isotherms	90
IIIA.4.1.Langmuir model	90
IIIA.4.2. Freundlich model	95
IIIA.4.3. Temkin model	98
IIIA.5. Mechanism of Adsorption	100
IIIB. Removal efficiency of heavy metal ions in waste water by Light white Brick Waste (LWBW)	101
IIIB.1. Characterization of Light white Brick	
Waste (LWBW)	101
IIIB.1.1. X-ray diffraction analysis	101
IIIB.1.2. Surface area and pore structure characteristics of LWBW	103
IIIB.1.3. Morphology and microstructures of	106
LWBW	100
IIIB.2. Factors Affecting the Removal Capacity	108
IIIB.2.1. Effect of contact time	108
IIIB.2.2. Effect of initial solution pH	110
IIIB.2.3. Effect of LWBW adsorbent mass	112
IIIB.2.4.Effect of initial heavy metal ions	114
concentration	117
IIIB.2.5. Competitive heavy metal ions	116
adsorption	
IIIB.3. Kinetic Models	118
IIIB.3.1. The Pseudo-first-order model	118

Title	Page
IIIB.3.2. The pseudo-second-order model	121
IIIB.3.3. The intra-particle diffusion model	121
IIIB.4. Adsorption Isotherms	124
IIIB.4.1.Langmuir model	124
IIIB.4.2. Freundlich model	128
IIIB.4.3. Temkin model	128
IIIB.5. Mechanism of Adsorption	131
IIIC. Removal efficiency of heavy metal ions in waste	132
water by Red Brick Waste (HOMRA)	132
IIIC.1. Characterization of Red Brick Waste (HOMRA)	132
IIIC.1.1. X-ray diffraction analysis	132
IIIC.1.2. Surface area and pore structure characteristics of HOMRA	134
IIIC.2. Factors Affecting the Removal Capacity	136
IIIC.2.1. Effect of contact time	136
IIIC.2.2. Effect of initial solution pH	138
IIIC.2.3. Effect of HOMRA mass	141
IIIC.2.4. Effect of initial heavy metal ions concentration	143
IIIC.2.5. Competitive heavy metal ions adsorption	145
IIIC.3. Kinetic Models	147
IIIC.3.1. The Pseudo-first-order model	147
IIIC.3.2. The pseudo-second-order model	150
IIIC.3.3. The intra-particle diffusion model	150
IIIC.4. Adsorption Isotherms	153
IIIC.4.1. Langmuir and Freundlich isotherms	153
Chapter IV: Summary and conclusions	156
References	167

List of Figures

	Dist of Figures	
Figure	Title	Page
1	XRD analysis of the DWTS fired at different temperatures (Q = quartz, I = Illite and A = Albite)	55
2	Adsorption isotherms types (IUPAC classification)	57
3	N ₂ adsorption-desorption isotherms of DWTS after thermal treatment at (a) 100°C, (b) 500°C and (c) 700°C	58
4	Pore size distribution of DWTS after thermal treatment at (a) 100°C, (b) 500°C and (c) 700°C	62
5	SEM micrographs of DWTS heated at (a) 100 °C, (b) 500 °C, (c) 700 °C and (d) EDX spectrum	65-66
6	Effect of firing temperature of DWTS on the removal percent of the heavy metal ions	68
7	Effect of contact time on the removal percent of the heavy metal ions	70
8	Effect of initial solution pH on the removal percent of the heavy metal ions	74
9	Effect of burnt DWTS adsorbent mass on the removal percent of heavy metal ions	76
10	Effect of initial heavy metal ions concentration on the removal percent of the heavy metal ions	78
11	Pseudo-first-order kinetic plots for (Pb, Cd and Ni) ions removal by the DWTS sample	83

Figure	Title	Page
12	Pseudo-second-order kinetic plots for (Pb, Cd and Ni) ions removal by the DWTS sample	86
13	Intra-particle diffusion plots for (Pb, Cd and Ni) ions removal by the DWTS sample	89
14	Langmuir sorption isotherm of (Pb, Cd and Ni) ions onto DWTS sample	92
15	Plot of dimensionless factor (R _L) versus concentration of the heavy ions	95
16	Freundlich sorption isotherm of (Pb, Cd and Ni) ions onto DWTS sample	97
17	Temkin sorption isotherm of (Pb, Cd and Ni) ions onto DWTS sample	99
18	XRD analysis of the LWBW (Q= quartz, CSH= calcium silicate hydrates, CS= calcium silicate, CaO= calcium oxide)	102
19	N_2 adsorption-desorption isotherms of LWBW	104
20	Pore size distribution of LWBW according to the BJH model applied on the desorption branch	105
21	SEM images of LWB sample showing; (a): Tobermorite and Quartz crystals, (b): Tobermorite and Wollastonite crystals and (c): EDX spectrum	106-107
22	Effect of contact time on the removal percent of the heavy metal ions	109

Figure	Title	Page
23	Effect of initial solution pH on the removal percent of the heavy metal ions	112
24	Effect of LWBW adsorbent mass on the removal percent of the heavy metal ions	113
25	Effect of initial heavy metal ions concentration on the removal percent of the heavy metal ions	115
26	Pseudo-first-order kinetic plots for (Pb, Cd and Ni) ions removal by the LWBW sample	119
27	Pseudo-second-order kinetic plots for (Pb, Cd and Ni)ions removal by the LWBW	122
28	Intra-particle diffusion plots for (Pb, Cd and Ni) ions removal by the LWBW sample	123
29	Langmuir sorption isotherm of (Pb, Cd and Ni) ions onto LWBW	125
30	Plot of dimensionless factor (R _L) versus concentration of (Pb, Cd and Ni) ions	127
31	Freundlich sorption isotherm of (Pb, Cd and Ni) ions onto LWBW	129
32	Temkin sorption isotherm of (Pb, Cd and Ni) ions onto LWBW	130
33	XRD analysis of the HOMRA (Q = quartz, Al = Alumunium oxide, M = Muliet, H = Hematite)	133
34	N_2 adsorption-desorption isotherms of HOMRA	135
35	Pore size distribution of HOMRA according to the BJH model applied on the desorption branch	136