UNIVERSITI PUTRA MALAYSIA

IMPROVEMENT OF ALGAL-ALGINATE BEAD STABILITY BY ZEOLITE MOLECULAR SIEVES 13X AND ITS APPLICATION IN BIOSORPTION

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By

SEYED AMIREBRAHIM EMAMI MOGHADDAM

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

September 2019

DEDICATION

This thesis is dedicated to

My lovely family: mother, father & sister

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 Doctor of Philosophy

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September 2019

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The interest in utilizing algae for wastewater treatment has been increased due to many advantages. Algae-Wastewater treatment system offers a cost-efficient and environmentally friendly alternative to conventional treatment processes. However, the recovery of free suspended algae from the treated effluent is one of the challenges during the treatment process. Therefore, the application of immobilized algae is a good approach to resolve the harvesting issue. Up to now, most of the algal immobilization has been done using cell entrapment method in which alginate (a natural polymer) has been applied as a carrier. Although alginate provides advantages in terms of biocompatibility, nontoxicity, cost-effectiveness, etc., this material has low stability to the chelating agents and a similar charge with cell surface of microorganisms, hence, it easily contributes to the leakage of large molecules due to the open lattice structure. Therefore, this study aims to improve the stability of *Chlorella*-Alginate Beads (CABs) by zeolite molecular sieves 13X (an aluminosilicate mineral with sodium ion) and further examined the potential use of the synthesized Zeolite 13X-Algal-Alginate Beads (ZABs) for copper biosorption from aqueous solution.

The immobilization was done via the entrapment of green living microalgae, *Chlorella vulgaris* within alginate/powdered zeolite 13X hydrogels. Cross-linking was carried out using 0.1 M $CaCl_2$ solution. The stability of the beads was tested by immersing them in a phosphate buffer solution at pH 7 as a chelating agent. Different process variables, including ratio of zeolite/alginate, pH and volume of beads were optimized using response surface methodology (RSM) to obtain the algal beads with high stability. Dissolution time of synthesized Zeolite-Algal-Alginate Beads (ZABs) in a chelating agent revealed a significant improvement on the beads stability (78.5 ± 0.5 min) compared to the control beads (51.5 ± 0.5 min) under the optimum conditions of zeolite/alginate (1.5:1), pH 5 and 2% of beads. Monitoring cell growth during 5 days of incubation showed good biocompatibility of zeolite 13X. Scanning electron microscopy (SEM) indicated rough surface and spherical shapes of ZABs. Brunauer-Emmett-Teller (BET) analysis revealed higher surface area for ZABs than other ABs. Energy dispersive

X-ray spectroscopy (EDX) and Fourier transform infrared spectroscopy (FTIR) of ZABs confirmed the presence of zeolite 13X within the matrix. The zeta potential value of ZABs (−23.33 ± 0.29 mV) indicated that the beads were relatively stable.

In addition, the potential use of ZABs for copper biosorption was evaluated and compared with Blank-Alginate Beads (BABs) and *Chlorella*-Alginate Beads (CABs). Different process parameters were investigated including contact time, pH and initial metallic ion concentration. It was found that the maximum biosorption capacity of ZABs was 85.88 mg/g biosorbent achieved at 180 min, pH 5 and initial metallic ion concentration of 150 mg/l whereas the maximum biosorption capacity of 70.02 and 77.32 mg/g biosorbent was obtained for BABs and CABs, respectively. ZABs showed higher stability than BABs and CABs in biosorption-desorption cycles. The kinetic and equilibrium data were analyzed via reaction/diffusion and Langmuir/Freundlich models, respectively. Scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDX) and Fourier transform infrared spectroscopy (FTIR) analyses revealed bonded metal ion to the ABs.

The findings of this research confirmed that modification of algal-alginate beads by zeolite molecular sieves 13X has the potential to improve the beads stability and their biosorption capacity.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENAMBAHBAIKAN KESTABILAN MANIK ALGA-ALGINAT OLEH PENAPIS MOLEKUL ZEOLIT 13X DAN KEGUNAANNYA DALAM PENJERAPAN BIO ION LOGAM

Oleh

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Kepentingan penggunaan alga untuk rawatan air sisa kian meningkat disebabkan oleh pelbagai manfaat. Sistem rawatan Alga-Air sisa menawarkan alernatif yang kos efektif dan mesra alam berbanding dengan proses-proses rawatan konvensional. Walaubagaimanapun, pemulihan alga terampai yang bebas daripada efluen yang telah dirawat merupakan salah satu cabaran semasa proses rawatan. Oleh itu, aplikasi alga pegun adalah pendekatan yang baik untuk mengatasi isu penuaian. Sehingga kini, kebanyakan alga pegun telah dilakukan menggunakan kaedah pemerangkapan sel dimana alginat (polimer semulajadi) telah digunakan sebagai pembawa. Walaupun alginat mempunyai banyak kelebihan dari segi biokompatibiliti, ketidaktoksikan, keberkesanan kos, dan lain lain, bahan ini mempunyai kestabilan yang rendah kepada agen pengkelat dan berkongsi cas yang sama dengan permukaan sel mikroorganisma, justeru, hal ini mudah menyumbang kepada kebocoran molekul-molekul yang besar disebabkan oleh struktur kekisi yang terbuka. Oleh itu, tujuan kajian ini adalah untuk menambah baik kestabilan manik-manik Chlorella-alginat dengan penapis molekul zeolit 13X (sejenis mineral aluminosilikat dengan ion sodium) dan untuk terus memeriksa keupayaan penggunaan manik-manik Zeolit 13X-Alga-Alginat yang telah disintesis untuk penjerapan bio kuprum daripada larutan berair.

Kaedah pegun telah dijalankan melalui pemerangkapan mikroalga hijau yang hidup, *Chlorella vulgaris* didalam gel-gel hidro alginat/serbuk zeolit 13X. Pautan silang telah dilakukan dengan menggunakan larutan $CaCl_2$ sebanyak 0.1 M. Kestabilan manik-manik telah diuji dengan merendamkam kesemuanya di dalam larutan penimbal fosfat pada pH 7 sebagai agen pengkelat. Proses pembolehubah-pembolehubah yang berbeza, termasuklah nisbah zeolit/alginat, pH dan bilangan manik-manik telah dioptimumkan menggunakan kedah gerak balas permukaan (RSM) untuk mendapatkan manik-manik alga yang mempunyai kestabilan yang tinggi. Masa pelarutan untuk manik-manik Zeolit-Alga-Alginat (ZABs) yang telah disintesis di dalam agen pengkelat menunjukkan penambahbaikan yang begitu signifikan untuk kestabilan manik-manik (78.5 ± 0.5 min)

berbanding dengan manik-manik kawalan (51.5 ± 0.5 min) pada keadaan-keadaan yang optimum untuk zeolit/alginat (1.5:1), pH 5 dan sebanyak 2% manik-manik. Pemonitoran pertumbuhan sel selama 5 hari masa inkubasi telah menunjukkan biokompatibiliti yang baik bagi zeolit 13X. Mikroskop pengimbas elektron (SEM) telah memperlihatkan permukaan yang kasar dan bentuk-bentuk sfera bagi ZABs. Analisis Brunauer-Emmett-Teller (BET) telah menunjukkan luas permukaan yang tinggi untuk ZABs berbanding dengan ABs yang lain. Spektroskopi Tenaga Penyerakan Sinar-X (EDX) dan Spektroskopi Inframerah Transformasi Fourier (FTIR) pada ZABs telah mengesahkan kehadiran zeolit 13X didalam matriks. Nilai keupayaan zeta untuk ZABs (−23.33 ± 0.29 mV) telah menunjukkan bahawa manik-manik tersebut adalah begitu stabil.

Tambahan lagi, keupayaan penggunaan ZABs sebagai penjerap bio untuk menyingkirkan ion logam kuprum dari larutan berair telah pun dinilai menggunakan manik-manik kawalan kosong-Alginat (BABs) dan manik-manik *Chlorella*-Alginat (CABs) sebagai sistem-sistem kawalan. Proses-proses parameter yang berbeza telah diselidik termasuklah waktu sentuh, pH dan kepekatan awal ion logam. Hal ini menemukan kapasiti penjerapan bio paling maksimum pada ZABs ialah 85.88 mg/g yang telah dicapai pada 180 minit, pH 5 dan kepekatan awal ion logam pada 150 mg/l manakala kapasiti penjerapan bio bagi BABs dan CABs, adalah masing-masing dicapai pada penjerap bio sebanyak 70.02 mg/g dan 77.32 mg/g. ZABs telah menunjukkan kestabilan yang lebih tinggi berbanding BABs dan CABs dalam kitaran-kitaran penjerapan bio-penyahjerapan. Data kinetik dan data keseimbangan masing-masingnya telah dianalisis melalui reaksi/serapan dan model-model Langmuir/Freundlich. Analisis-analisis Mikroskopi pengimbas elektron (SEM), Spektroskopi Tenaga Penyerakan Sinar-X (EDX) dan Spektroskopi Inframerah Transformasi Fourier (FTIR) telah mendedahkan keterikatan ion logam kepada ABs.

Penemuan-penemuan melalui kajian ini telah mengesahkan bahawa pengubahsuaian bagi manik-manik alga-alginat oleh penapis molekul zeolit 13X mempunyai keupayaan untuk menambah baik kestabilan manik-manik dan kemampuan penjerapan bio mereka.

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LIST OF ABBREVIATIONS/GLOSSARY OF TERMS

Abbreviation	**Definition**
AAS	Atomic Absorption Spectrophotometer
ABs	Alginate Beads
ANOVA	Analysis of Variance
ATR	Attenuated Total Reflectance
BABs	Blank-Alginate Beads
BC	Biomass Concentration
BET	Brunauer-Emmett-Teller
CABs	*Chlorella*-Alginate Beads
CCD	Central Composite Design
EDX	Energy Dispersive X-ray Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
OD	Optical Density
RSM	Response Surface Methodology
SEM	Scanning Electron Microscopy
WC	Water Content
ZABs	Zeolite 13X-Algal-Alginate Beads

Glossary	**Definition**	
A	Code of ratio of zeolite/alginate	
b	Langmuir model Constant	(l/mg)
B	Code of pH	
C	Code of volume of beads	(%)
C_0	Initial metal ion concentration	(mg/l)
C_e	Concentration of metal ion at equilibrium	(mg/l)
D	Weight of dried sample	(g)
I	Diffusion model constant	
k_1	Rate constant of pseudo-first order biosorption	(min^{-1})
k_2	Rate constant of pseudo-second order biosorption	[g/(mg min)]
k_d	Intraparticle diffusion rate constant	[mg/(g $min^{0.5}$)]
K_F	Freundlich model constant	[(mg/g) $(mg/l)^n$]
m	Amount of biosorbent	(g)
n	Freundlich model exponent	
q	Biosorption capacity	(mg/g)
q_e	Biosorption capacity at equilibrium	(mg/g)
q_m	Maximum theoretical biosorption capacity	(mg/g)
q_t	Biosorption capacity at time of *t*	(mg/g)
R^2	Correlation coefficient	
R_L	Dimensionless separation factor	
Std	Standard order	
t	Time	(min)
V	Solution volume	(l)

W	Weights of wet sample	(g)
Y	Code of dissolution time	(min)

CHAPTER 1

INTRODUCTION

1.1 Background of study

Water is the basic element of life on earth. The demand for water in the entire world is growing fast for domestic, agricultural and industrial activities. However, the availability and quality of water resources face severe threats due to the industrialization and rapid economic development, hence, producing a huge amount of wastewater. This wastewater contains organics, suspended solids and hazardous materials such as heavy metals which are not biodegradable. These materials tend to accumulate in organisms and potentially cause severe contamination and diseases (Inglezakis, Loizidou, & Grigoropoulou, 2003; Kwakye, McMinimy, & Aschner, 2016). Hence, wastewater treatment is essential to prevent deterioration of the environment and solve the issue of water shortage and health.

Wastewater treatment consists of removing or decreasing a number of hazardous substances such as chemicals and biological pollutants (Eroglu, Smith, & Raston, 2015). The selection of the treatment approaches is strongly influenced by their characteristics and compositions. Various wastewater treatment approaches have been used such as chemical, physical and biological (Eroglu et al., 2015). Advanced oxidation, electrocoagulation and flocculation are the most common methods of physical and chemical treatment whereas suspended or activated sludge process is an example of the biological treatment that is widely applied (Das & Adholeya, 2015). Although these conventional methods have successfully treated various wastewater sources, they have some limitations. The physical and chemical methods have the problems of high-energy requirements, incomplete removal of heavy metals, generation of secondary pollutants, complex operation, and high cost (Das & Adholeya, 2015; Krishnani, Meng, Christodoulatos, & Boddu, 2008; Quintelas et al., 2009), whereas biological method deals with the problems of the easy washout and low biomass concentration (Das & Adholeya, 2015). To overcome the issues, the use of microalgae to treat wastewater is currently of global interest due to its advantages.

Microalgal cells have the ability to uptake nutrients such as phosphorus, nitrogen and ammonium as well as heavy metals to reduce BOD in wastewater (Abdel-Raouf, Al-Homaidan, & Ibraheem, 2012; Aziz & Ng, 1992; Phang & Ong, 1988; Sydney et al., 2011) and also simultaneously capture carbon dioxide from the atmosphere during photosynthesis, hence, decreasing the greenhouse gaseousness (Zeng, Danquah, Chen, & Lu, 2011; Zeng et al., 2012). Also, the wastewater can be considered as a cheaper nutrient source for the growth of microalgae. However, at the current state, the biological nutrient removal technologies, including the use of microalgae, have not been yet to be competitive in the wastewater industries. The main issue in integrating algae with wastewater treatment contributes to the high cost of recovery of the treated effluent and biomass using current dewatering methods such as centrifugation and filtration (Zeng et al., 2012). As an option, the existing cell suspended method can be replaced with immobilization method. Not only cell immobilization simplify the separation process, but it also offers other advantages such as higher cell density, higher productivity, better cell stability, and biomass recirculation (Das & Adholeya, 2015; Djukić-Vuković, Jokić, Kocić-Tanackov, Pejin, & Mojović, 2016; Eroglu et al., 2015; Idris & Suzana, 2006; Vasilieva, Lobakova, Lukyanov, & Solovchenko, 2016).

One of the most important parts of the immobilization technique is selecting a suitable carrier. Literature show that most of the algal immobilization are carried out using cell entrapment method in which alginate (a natural polymer) has been applied as a carrier (Bayramoglu & Arıca, 2009; Bayramoğlu, Tuzun, Celik, Yilmaz, & Arica, 2006; da Costa & Leite, 1991; Kondo, Hirayama, & Matsumoto, 2013; Mallick & Rai, 1993; I. Moreno-Garrido, Campana, Lubián, & Blasco, 2005; Petrovič & Simonič, 2016; Rai & Mallick, 1992; Shen, Gao, & Li, 2017; Wan Maznah, Al-Fawwaz, & Surif, 2012; Wilkinson, Goulding, & Robinson, 1990). The reason that researchers tend to use alginate for the immobilization of microalgae is due to its advantages, including biocompatibility, simple preparation, cost-effectiveness, and nontoxicity (Desmet et al., 2015; I. Moreno-Garrido et al., 2005; Petrovič & Simonič, 2016). Zhang et al. synthesized a biocompatible hybrid matrix for the encapsulation of *Chlamydomonas reinhardtii* through modifying the composition (alginate, polycation and silica). They reported good chemical stability to chelating agents for the hybrid beads (Zhang, Wang, Charles, Rooke, & Su, 2016). In another study, Desmet et al. synthesized highly porous (Ca-alginate-SiO_2-polycation) shell:(Na-alginate-SiO_2) core hybrid beads for the encapsulation of *Dunaliella tertiolecta*. The authors reported durability of the beads (Desmet et al., 2015). Also, Pannier et al. developed alginate/silica hybrid materials for the immobilization of *Chlorella vulgaris*. They reported an improvement to the stability in salt-containing solutions compared to alginate gels using Ca^{2+}-ions (Pannier, Soltmann, Soltmann, Altenburger, & Schmitt-Jansen, 2014).

Zeolite is another material that can be an appropriate candidate for the modification of algal-alginate beads. Zeolites are inorganic silica materials (Sakaguchi, Matsui, & Mizukami, 2005) classified into three groups of natural, modified and synthetic (Yuna, 2016). They are widely applied as ion exchangers, catalysts (Sakaguchi et al., 2005), and also as a support for biomass immobilization (Al-Hassan et al., 1991; Corona-González et al., 2014; Djukić-Vuković et al., 2016; Djukić-Vuković, Mojović, Jokić, Nikolić, & Pejin, 2013; Fernández et al., 2007; Figueroa-Torres et al., 2016; Lameiras, Quintelas, & Tavares, 2008; Mery et al., 2012; Pazos, Branco, Neves, Sanromán, & Tavares, 2010; Quintelas et al., 2009; Shindo, Takata, Taguchi, & Yoshimura, 2001; Weiß et al., 2010) because of their characteristics, including suitable thermostability performance, resistance to microbial degradation, and cost-effectiveness (Das & Adholeya, 2015; Zhou, Li, An, Fu, & Sheng, 2008).

Zeolite molecular sieves 13X is a type of synthetic zeolites that its structure involves silica, alumina and sodium ions. Sodium ions along with silica can help to improve the stability of the beads. Furthermore, the existence of sodium ions can make the zeolite 13X surface positively charged (Djukić-Vuković et al., 2013); hence, it can make the alginate matrix less negative compare to the common type resulting in more algal cell affinity to diffuse into the gel matrix reducing cell leak out from the matrix. Furthermore, because of its ion exchange capacity and microporous structure, zeolite 13X can attend in metal sorption process along with algal-alginate matrix resulting in an improvement in sorption capacity.

This study investigates the stability of algal-alginate beads by modifying the matrix by zeolite molecular sieves 13X. The optimization of process variables and evaluation of kinetic and equilibrium models are included in this study. Lastly, the examination of the synthesized beads in metallic biosorption process are carried out to determine its effectiveness.

1.2 Problem statement

There are some problems on the way of using alginate for cell immobilization. Alginate beads have low stability to the chelating agents, hence, they contribute to the leakage of large molecules due to the open lattice structure (Smidsrod & Skjak-Braek, 1990; Zhang et al., 2016). Furthermore, the alginate matrix has a negative charge (Pannier et al., 2014; Smidsrod & Skjak-Braek, 1990) and the cell surface of microorganisms such as *Chlorella* has also a negative charge (comes from dissociation of some groups such as uronic acid and/or sulfate groups) (Eroglu et al., 2012) that do not easily diffuse into the gel matrix. Although in case of successful immobilization, the cells tend to leak out from the matrix. In order to overcome the stability drawback, the alginate matrix has been modified with silica by researchers, and their findings showed the good potential of silica to improve the stability (Desmet et al., 2015; Pannier et al., 2014; Zhang et al., 2016).

In this study, algal-alginate beads were modified by zeolite molecular sieves 13X to overcome drawbacks of low stability and less cell affinity for the immobilization of green living microalgae, *Chlorella vulgaris*. Furthermore, the feasibility of the beads for the biosorption of Cu^{2+} metal ion from aqueous solution was investigated. The main reason for the selection of copper metal ion was due to the fact that it is among the most toxic pollutants that potentially cause serious problems such as kidney damage, anaemia, etc. when expose to humans. The main copper sources in industrial wastewaters involve petroleum, mining, fertilizers, electroplating, metal cleaning plating baths, pulp and paper industries (Al-Rub, El-Naas, Ashour, & Al-Marzouqi, 2006). Thus, treatment of water resources polluted with copper metal ion is vital.

1.3 Research objectives

This study is designed to achieve the following objectives:

a) To investigate the stability of algal-alginate beads by modifying the matrix using zeolite molecular sieves 13X
b) To optimize the process variables of the algal beads using response surface methodology (RSM) to obtain the beads with high stability
c) To examine the biosorption capacity of the synthesized algal beads in metallic process
d) To evaluate the kinetic and equilibrium models of biosorption process by the algal beads

1.4 Scope of the study

1.4.1 Investigation of the algal beads stability

The algal beads stability was investigated by immersing them in a chelating agent along with their characterizations through zeta potential, scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET), energy dispersive X-ray spectroscopy (EDX), and Fourier transform infrared spectroscopy (FTIR).

1.4.2 Optimization of process variables of the algal beads

In order to find the optimum formulation for the synthesis of the algal beads with high stability, response surface methodology (RSM) was used in which the variables were ratio of zeolite/alginate (0.5:1, 1:1 and 1.5:1), pH (5, 7 and 9) and volume of beads (2, 6 and 10 %) with the response of dissolution time in a chelating agent.

1.4.3 Examination of the biosorption capacity of the algal beads

The synthesized algal beads were applied for the copper metal biosorption from aqueous solution. The effects of different operational parameters, including contact time (0-240 min), pH (3-6) and initial metallic ion concentration (5-200 mg/l) on the biosorption capacity of the metal ion were investigated. SEM, EDX and FTIR analyses were used for the beads characterization in biosorption studies.

1.4.4 Evaluation of kinetic and equilibrium models

The kinetic and equilibrium models of the biosorption process by the algal beads were evaluated through experimental data. The kinetic data were analyzed by reaction (pseudo-first and pseudo-second order) and diffusion models. The equilibrium data were studied via Langmuir and Freundlich models.

1.5 Significance of the study

This study modifies *Chlorella*-alginate beads by zeolite molecular sieves 13X to improve the algal matrix stability, its cell affinity and the metal sorption capacity. The findings of this research have a significant impact on various applications such as municipal and/or industrial wastewater treatment processes where the improved stability and biosorption capacity of algal-alginate beads is essential.

1.6 Structure of the thesis

There are five chapters in this thesis of which each chapter explains the sequence of the research:

Chapter 1 presents the background on the subject, problem statement, research objectives, scope of the study (including investigation of the algal beads stability, optimization of process variables of the algal beads, examination of the biosorption capacity of the algal beads, and evaluation of kinetic and equilibrium models), significance of the study, and structure of the thesis.

Chapter 2 covers literature review on the subject including the following parts: immobilization (types of immobilization, operational modes of immobilization and ideal carrier for immobilization), algal immobilization (microalgae and its applications, immobilization of algal biomass and biosorption process and its mechanism), zeolite and its application in biotechnology (zeolite and its classification and applications of zeolite), and potential application of zeolite 13X to modify algal-alginate beads.

Chapter 3 involves the materials and methods describing the experimental procedure in the current research. This chapter has been divided into two sections. The first section is related to synthesize of the beads, including preparation of zeolite molecular sieves 13X, microalgae and culture conditions (preparation of medium and cultivation of *Chlorella vulgaris*), preparation of immobilized microalgae beads (preparation of *Chlorella* suspension and beads preparation), analytical procedures and characterization studies (including cell growth and the number of viable cells, stability test, surface charge, morphology of the samples, surface area of the samples and Fourier transform infrared spectroscopy (FTIR)), and experimental design for immobilization studies. The second section is related to biosorption studies, involving preparation of metal ion stock solution, the effect of different parameters on the biosorption process, desorption and reusability, biosorption capacity, kinetic and equilibrium models, and analytical procedures and characterization studies (including determination of metal ion concentration, water content, SEM-EDX, and Fourier transform infrared spectroscopy).

Chapter 4 presents the results and discussion of the two sections mentioned in chapter 3. Section Ⅰ covers characterization of the beads (including zeta potential, surface morphology, surface area and FTIR spectral analysis), statistical analysis (analysis of variance (ANOVA) and optimum conditions) and evaluation of biocompatibility of zeolite 13X. Section Ⅱ describes effects of contact time, initial pH and initial metal ion concentration on metal ion biosorption. Also, biosorption-desorption cycles, biosorption kinetic models (involving reaction (pseudo-first and pseudo-second order) and diffusion based models) and biosorption equilibrium models (Langmuir and Freundlich models), and characterization of the biosorbents (including water content, SEM-EDX and FTIR spectral analyses) were presented.

Chapter 5 refers to general conclusions based on the findings achieved in the results and discussion. Also, recommendations for future studies were presented in this chapter.

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LIST OF PUBLICATIONS

Publications

Emami Moghaddam, S. A., Harun, R., Mokhtar, M. N., & Zakaria, R. (2019). Kinetic and equilibrium modeling for the biosorption of metal ion by Zeolite 13X-Algal-Alginate Beads (ZABs), *Journal of Water Process Engineering*, Under Review.

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