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THE KINETICS AND MECHANISM OF LEAD (II) ADSORPTION IN DIFFERENT TYPES OF CONTACTOR BY POWDERIZED RHIZOPUS OLIGOSPORUS

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By

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Alhamdulillah

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B	BET isotherm coefficient relating adsorption energy (J/g.mol)
C_{eq}	Adsorbate concentration (residual) at equilibrium (mg/L)
C_o	Initial adsorbate concentration (mg/L)
C_s	Saturation concentration (solubility limit) of the solute (mg/L)
C_f	Final concentration of solution (mg/L)
D	Pore diffusion coefficient (m^2/min)
D_t	impeller diameter (m)
E	Polanyi potential
E_a	Activation energy (cal/mol).
E_1	Heat of adsorption
E_2	Heat of condensation
ΔH^o	enthalpy
K	Fluid consistency coefficient (Pa.S^n)
k	Constant in Arrhenius equation; rate constant
K_{ad}	Constant in Lagergren equation; equilibrium rate constant of sorption (1/min)
K_d	Constant in equation for Langmuir Isotherm; energy of adsorption (L/g)
K_f	Constant in equation for Freundlich Isotherm; adsorption capacity (mg/g)
K_p	Intraparticle diffusion rate constant. (mg/g/$min^{0.5}$)
log (x)	logarithm (x) to the base 10
ln (x)	logarithm (x) to the base e
N	impeller speed, rpm (s^{-1})
pH	Hydrogen potential
Q	Experimetal maximum metal adsorbed (mg/g)
Q	Constant in equation for Langmuir Isotherm; maximum metal adsorbed (mg/g)
q	Amount of adsorbate adsorbed at time t (mg/g)
q_o	Amount of adsorbate adsorbed per unit weight of adsorbent at the beginning of adsorption process (mg/g)
q_{eq}	Amount of adsorbate adsorbed per unit weight of adsorbent equilibrium (mg/g)
R	Universal gas constant (8.31 J/mol/K)
R^2	Correlation coefficient
Re	Reynolds Number, $ND_t^2\rho/\mu$
r_o	Radius of sorbent (m)
ΔS^o	entropy
T	Absolute temperature (^oK = 273 + ^oC)
t	Time (minute)
V_o	Volume of solution in the contactor (L)
X_o	Amount or weight of adsorbent in the contactor (g).

Greek

μ	Absolute liquid viscosity (kg/m.s.)
μ_{app}	Apparent liquid viscosity (cP)
λ	Shear rate (s^{-1})
ρ	Liquid density (kg/m^3)
τ	is the shear stress (D/cm^2)

Subscripts

max	maximum
ad	adsorption
app	apparent

Superscript

n	Constant in equation for Freundlich Isotherm; adsorption intensity (dimensionless)
n	is the flow behaviour index (dimensionless)

Abstract of a thesis submitted to the Senate of Universiti Putra Malaysia as fulfillment of the requirements for the degree of Master of Science

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MAIZIRWAN MEL

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Chairman : Associate Professor Dr. Arbakariya Ariff

Faculty : Food Science and Biotechnology

The effect of sorption conditions on the rate and capacity of lead uptake by powderized biomass of *Rhizopus oligosporus* was first carried out in shake flask experiments. Lead sorption by *Rhizopus oligosporus* was also investigated in different types of contactor such as stirred tank bioreactor, airlift fermenter and packed-bed column. The experimental data of lead adsorption in different sorption conditions (pH, temperature, solution viscosity, lead and biomass concentration) and different operating variables of the contactor (agitation speed and air flowrate) were analysed using Langmuir and Freundlich sorption isotherm models. The mechanism of lead uptake by the cell was examined using TEM micrograph, EDXA and FTIR photoacoustic.

The experimental data of lead sorption by *Rhizopus oligosporus* fitted well to Langmuir and Freundlich sorption isotherm models, indicating that the sorption was similar to that for ion-exchange resin. This means that the sorption is a single layer metal adsorption which occured as a molecular surface coverage. This assumption was confirmed by the examination of lead sorption using TEM micrograph, EDXA and FTIR photoacoustic, which showed that during sorption most of lead was adsorbed on the surface of cell.

From shake flask experiment, it was found that the biomass concentration and initial solution pH optima for lead sorption at initial lead concentration ranging from 50-200 mg/L was 0.5 g/L and pH 5, respectively. In term of the ratio of initial lead concentration to biomass concentration, the optimum value for lead sorption was 750 mg/g. In all types of contactor investigated, maximum lead uptake capacity increased with increasing temperature and drastically decreased with increasing solution viscosity. Lead adsorption kinetic parameters values, calculated using Langmuir and Freundlich models, were significantly varied with sorption condition. Intraparticle diffusion rate constant (K_p) and equilibrium adsorption rate (K_{ad}) decreased with increasing solution viscosity, while diffusion coefficient (D) increased with increasing solution viscosity. On the other hand, D was decreased with increasing temperature while K_{ad} was not significantly different at different temperatures. When 5 L stirred tank bioreactor was used as a contactor, the highest lead uptake capacity was obtained at agitation speed ranging from 50-150 rpm (Re = 3,900 - 11,700). On the other hand, the optimum air flowrate for lead sorption in 2 L airlift fermenter was obtained at 2 vvm. Increased in the degree of turbulence as created by increased in degree of agitation (stirred tank bioreactor) and air flowrate (airlift fermenter), significantly reduced K_{ad} and D but has no effect on K_p.

The maximum lead uptake capacity obtained in shake flask, stirred tank bioreactor and airlift fermenter at optimum sorption conditions was 126, 79 and 74 mg/g, respectively. Absolute removal of lead ions from solution was achieved when fixed packed-bed column was used as a contactor. However, the maximum lead uptake capacity (24 mg/g) was 3 times lower than that obtained in stirred tank bioreactor or an airlift fermenter.

Abstrak thesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan Ijazah Master Sains

KINETIK DAN MEKANISMA PENJERAPAN PLUMBUM PADA JENIS KONTAKTOR YANG BERBEZA OLEH SERBUK *RHIZOPUS OLGOSPORUS*

OLEH

MAIZIRWAN MEL

MAC 1998

Pengerusi : Professor Madya Dr. Arbakariya Ariff

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Kesan keadaan serapan keatas kadar dan keupayaan pengambilan plumbum oleh serbuk *Rhizopus oligosporus* pada permulaannya dijalankan dalam kelalang penggoncang. Penjerapan plumbum oleh *Rhizopus oligosporus* juga dikaji menggunakan pelbagai jenis kontaktor seperti bioreaktor tangki pengaduk, fermenter turus-udara dan turus 'packed-bed'. Data-data eksperimen penjerapan plumbum pada keadaan serapan yang berbeza (pH, suhu, kelikatan larutan, kepekatan plumbum dan biojisim) dan pembolehubah operasi kontaktor yang berbeza (kelajuan pengadukan dan kadar alir udara) dianalisa dengan menggunakan model isoterm serapan Langmuir dan Freundlich. Mekanisma pengambilan plumbum oleh sel ditentukan dengan menggunakan mikrograf TEM, EDXA dan fotoakustik FTIR.

Data eksperimen penjerapan plumbum oleh *Rhizopus oligosporus* cekuk (bersesuaian) terhadap model isoterm Langmuir dan Freundlich, membuktikan bahawa penjerapannya adalah sama dengan resin penukar ion. Ini menunjukkan bahawa penjerapannya adalah penjerapan oleh lapisan tunggal yang dikenali sebagai penutup permukaan molekul. Anggapan ini dibuktikan oleh penentuan penjerapan plumbum dengan menggunakan mikrograf TEM, EDXA dan fotoakustik FTIR yang menunjukkan penjerapan plumbum adalah terjadi pada permukaan sel.

Dari eksperimen menggunakan kelalang bergoncang, kepekatan biojisim dan pH optimum larutan awal pada selang kepekatan plumbum awal 50-200 mg/L adalah diperolehi masing-masing pada 0.5 g/L dan pH 5. Nisbah kepekatan plumbum awal kepada kepekatan biojisim, yang optimum untuk penjerapan plumbum adalah pada 750 mg/g. Untuk semua jenis kontaktor yang dikaji, keupayaan pengambilan plumbum maksima adalah meningkat dengan kenaikan suhu dan menurun secara drastik dengan kenaikan kelikatan larutan. Nilai parameter kinetik penjerapan plumbum yang telah dikira dengan menggunakan model penjerapan Langmuir dan Freundlich, menunjukkan perbezaan yang nyata dengan keadaan serapan. Angkatap kadar difusi antara partikel (K_p) dan kadar penyerapan pada keseimbangan (K_{ad}) adalah menurun dengan kenaikan kelikatan larutan, sedangkan angkali difusi (D) adalah meningkat dengan kelikatan larutan. Disamping itu, D adalah menurun dengan kenaikan suhu sedangkan perbezaan K_{ad} tidak nyata pada suhu yang berbeza. Apabila bioreaktor tangki pengaduk 5 L digunakan sebagai kontaktor, keupayaan pengambilan plumbum tertinggi diperolehi pada kelajuan pengadukan diantara 50 hingga 150 rpm (*Re* = 3,900 - 11,700). Ini bermakna, kelajuan pengaliran udara optimum untuk penjerapan plumbum di dalam fermenter airlift 2 L diperolehi pada 2 vvm. Peningkatan kadar gelora yang dihasilkan dengan peningkatan kadar pengadukan (bioreaktor tangki pengaduk) dan kadar alir udara (fermenter turus-udara) menurunkan K_{ad} dengan nyata tetapi tidak mempengaruhi K_p.

Keupayaan pengambilan plumbum maksima yang diperolehi di dalam kelalang pengguncang, bioreaktor tangki pengaduk dan fermenter airlift pada keadaan penjerapan optimum adalah masing-masing 126, 79 dan 74 mg/g. Pengasingan mutlak ion plumbum dari larutan diperolehi jika turus 'packed bed' digunakan sebagai kontaktor. Bagaimanapun, keupayaan pengambilan plumbum maksima (24 mg/g) adalah tiga kali lebih rendah daripada yang diperolehi dalam bioreaktor tangki pengaduk dan fermenter airlift.

CHAPTER I

INTRODUCTION

Environmental pollution due to wastewater containing lead has recently become a serious problem. Lead has been known for its toxicity and hazardous effect to human for a long time. The main indicator of lead poisoning in humans is the content of this element in whole blood (Volesky, 1990a). Toxicity of lead usually affect the gastrointestinal track, or the nervous system and sometime both (Orumwense, 1996). The presence of lead in the environment possess a significant health risk to human, especially to children (Mielke et al., 1983; Lajis, 1996; Hynes and Jonson, 1997).

Lead is widely used as an industrial raw material for storage battery manufacturing, printing, pigments, fuels, photographic materials, matches, explosive manufacturing, lead soldered cans, and water pipes (Akzu and Kutsal, 1991; Niu et al., 1993; Kuyucak et al., 1994; Kim et al., 1995; and Orumwense, 1996). The accelerated rate of industrialization has positively increased the number of polluting sources in effluent.This form of industrial effluent is discharged into the environment annually, directly or indirectly. Department of Environment in Malaysia has estimated that 109,906 tons of wastewater containing heavy metals are discharged yearly. The Federal Territory and Selangor accounted for 39,302 tons and 46,348 tons per annum, respectively

(Leng, 1997). Unlike organic pollutants which are susceptible to biological degradation, lead and other heavy metals released to the environment can be toxic because it will not be degraded into harmless products. Therefore, the treatment of wastewater containing soluble heavy metals is important for public health.

Traditional physical and chemical treatment methods have been proven to be inefficient in the removal of metal pollutants from hazardous waste and does not generally allow strict regulatory requirements to be met. These methods include chemical precipitation, electrode deposition, and ion exchange (Niu et al., 1993). The need for economical, effective and save methods for removing heavy metal from wastewater has resulted in the search for unconventional materials that may be useful in reducing the level or accumulation of heavy metals in the environment. The failure of conventional methods to overcome the problem of heavy metals pollution has prompted people to turn to bio-treatment. In the last few years, biosorption of heavy metals has been recognized as a potential alternative to existing technologies for removing heavy metals from their external environment. Application of biosorption technology for the treatment of wastewater containing heavy metals has been given significant attention recently by the research community.

The newly discovered metal sequestering properties of certain types of microbial biomass and algae offer considerable promise (Volesky, 1990b). The accumulation of metals by fungal biomass had received more attention in recent years because of its potential in environment protection (Tsezos, 1984). The potential use of fungi such as *Penicillium chrysogenum* (Niu et al., 1993), *Aspergilus niger* (Kim et al., 1995), *Aureobasidium pullulans* (Suh et al., 1996) as biosorbent for lead adsorption from effluent have been investigated. New biosorbents for toxic lead, cadmium, zinc and uranium based on cell biomass have been in the focus of interest and should be tested in detoxification of metal-bearing industrial effluents. The use of dead residues of microorganism produced by the fermentation industries, can be economical alternative method to depollute the effluents from heavy toxic metals. Reports on the potential use of other industrial fungi such as *Rhizopus oligosporus, Aspergillus flavus* and *Aspergillus awamori* in removing lead and other metals from the solution is scarce.

Quantitative evaluation is essential for comparison and evaluation of the performance of biosorbents in a metal-sorption process. Better understanding of metal biosorption mechanisms is essential for process optimization which can be achieved through meaningful and pragmatic modelling of the biosorption system. Several generations of original mathematical models of biosorption processes have been proposed and are further tested for their potential to predict the uptake of metal ions. For example, the evaluation of continuous-flow sorption column systems requires combination of hydraulic, mass transfer and reaction aspects. Technologically meaningful models of these systems become very sophisticated and represent a powerful tool in process engineering.