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BIOSORPTION DYNAMICS OF CADMIUM(II) IN A PACKED-BED COLUMN USING IMMOBILIZED *Spirogyra subsalsa sp*: A GREEN APPROACH TO WASTEWATER TREATMENT

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ABSTRACT

This research aims to study the biosorption of cadmium(II) by green algae *S. subsalsa* biomass immobilized in sodium silicate (IMSB) using the continuous packed-bed column method. The effects of various parameters, such as flow rate, influent pH, and influent metal concentration, were investigated. In general, there is no difference between pure S. subsalsa biomass (PSB) and IMSB in terms of functional groups, as shown by the IR spectra. The biosorption process is a rapid process, wherein more than 50% of the final uptake value occurs at a rate of 0.5 mL/minute. The biosorption capacities of biomass for cations increase rapidly between pH 2.0–3.0, and then the maximum sorption was seen at pH 4.0. The biosorption capacity increased with initial concentration in the range 50–200 mg/L. A comparison of the biosorption of cadmium(II) by IMSB showed an increase in uptake of over 8.84%. The immobilized biomass could be regenerated using nitrate acid and proportional with the amount of nitrate acid concentration, with up to cadmium(II) recovery more than 80% by HNO_3 0.5 M. This study suggests that such an immobilized biosorbent system has the potential to be used in the industrial removal and recovery of cadmium(II) from aqueous solution.

Keywords: *Spirogyra subsalsa sp.*, biosorption, Cd(II), biosorption capacity, column method, immobilization

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INTRODUCTION

Several toxic heavy metals, like chromium, nickel, copper, zinc, cadmium, lead, mercury, and arsenic, are some of the most common metals that can be found in contaminated water.[1] Of all metals, cadmium is presents in almost human activities; anthropogenic sources including mining, smelting, fertilizers and pesticides usage, and combustion of fossil fuels have escalated cadmium presence in the environment.[2] Cadmium has high mobility since its soluble in aqueous solutions, as Cd^{2+} ions, and can be influenced further by pH, ionic strength, and redox state of the solution.[3] It also has a long biological half-life, around 10 to 30 years.[4] In general, humans are exposed to cadmium by ingestion, respiration, inhalation, and dermal resorption.[5] Biosorption is part of adsorption techniques, which involves adsorbates bound to the surface of biological matrices and is highly regarded as eco-friendly[6]. Extensive research has been conducted on a wide range of materials, including microbial biomass (bacteria, yeast, fungi) and algae.[7] Spirogyra, commonly known as water silk or pond scum, is a genus comprised of freshwater green algae species. It can be found floating in tropical ponds and pools they characterized by their apparent green color and slimy look. While proven to be effective, free biosorbent does not offer mechanical stability and regeneration due to how fragile dead microbial cells are in general. Biosorption by immobilized algal biomass, especially by the continuous column method, is determined by a few factors, such as pH, the amount or dosage of biosorbent, contact time, flow rate, and column size.[8] This study aims to measure several parameters that affect the biosorption of cadmium(II) by *Spirogyra subsalsa sp.,* a green algae species, immobilized in silicate matrices. The measured parameters are flow rate, metal concentration, eluting acid concentration, and its recovery percentage.

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EXPERIMENTAL

Material

Cadmium(II) cation stock solution with a concentration of 1000 mg/L, HNO_3 or NH_3 solution for pH adjustment. Sulfuric acid (5%), sodium silicate solution (6%), barium chloride.

Preparation of Biosorbents

Green algae S. subsalsa biomass was obtained from the waters of Batang Air Dingin River, Lubuk Minturun, Padang, West Sumatra, Indonesia. The collected algae were separated from their growth media, and then a small batch was separated for identification. The algae were washed and rinsed with deionized water, and then dried in the open air (without direct sunlight). The dried biomass was soaked in a 1% v/v nitric acid solution for one hour, then washed and rinsed with distilled water until the washing water was clear. After that, the algae biomass was dried again in the same way until a constant weight was obtained. The pure biomass particles obtained were stored in a desiccator.

Immobilization of Biosorbents

75 mL of 5% sulfuric acid was mixed with 6% sodium silicate solution to obtain a pH of 2.0, then 5 g of biomass was added to the mixture, stirred for about 15 minutes. Then, 6% sodium silicate solution was added gradually until the pH of the mixture reached 7.0. The polymer formed was washed with sufficient water until 2 drops of $BaCl_2$ solution were added, and no white precipitate was formed. The polymer gel that immobilized the biomass was dried overnight at a temperature of 60°C, then ground to a particle size of 250 μm.[9]

Continuous Column Methods

A glass column with a diameter of 1.0 cm, equipped with other necessary equipment, was prepared, then packed with 1.0 g of IMSB. In each optimization treatment, 25 mL of metal solution with a certain concentration and pH was passed through the column at a certain flow rate. The eluent coming out of the column was collected, and then the metal concentration was determined by AAS with air-acetylene flame at a wavelength of 283.3 nm. The difference between the metal concentration in the eluent and the initial concentration is the amount of metal ions absorbed by the biomass. The amount of metal absorbed is expressed as the weight (in mg) of metal absorbed per weight (in grams) of biosorbent used. Regeneration of the used column, containing adsorbed metal, was achieved by continuously eluting 10 mL of nitric acid solution, HNO_3. The eluent obtained was collected, and the desorbed metal content was determined using AAS.

Characterization

Semi-quantitative analysis of dry biomass of pure green algae *S. subsalsa* was analyzed by Energy Dispersive X-ray Analysis (EDX), and functional groups in the biosorbent were identified by Fourier Transform Infrared Spectroscopy (FTIR).

Absorption Studies

The concentration of metals at equilibrium (which remain in solution) and the initial concentration of lead were determined by AAS. The amount of metal absorbed by biomass is the difference between the concentration of metal at equilibrium and the initial concentration of metal (Hancock, 1996b). The amount of metal absorbed is expressed as the weight (mg) of metal absorbed per weight (g) of biosorbent used. The linear form of the Langmuir isotherm equation is expressed as:[9]

$$\frac{1}{a} = \frac{1}{a_m K}\frac{1}{C} + \frac{1}{a_m}$$

Recovery (R) is a value that shows what portion of the absolute amount of trace elements is contained in the concentrate, which is expressed by:

$$R(\%) = \frac{q_c}{q_s} \times 100\%$$

RESULTS AND DISCUSSION

Characterization of Biosorbents

Semi-quantitative analysis data of the main elements of IMSB using Energy Dispersive X-ray Analysis (EDX) as in Fig.-1, while the complete composition and when compared with pure biomass, as shown in Table-1. The surface morphology of PSB compared with IMSB observed by Scanning Electron Microscopy (SEM) as seen in Fig.-2 and Fig.-3, respectively. SEM photo images show that biomass immobilization with sodium silicate causes morphological changes on the surface, and biomass turns into denser grains than pure biomass. IMSB biosorbent showed quantitative changes of several elements, especially silicon, from 0.58% in pure biomass to 9.97% in immobilized biomass. It was also seen that there was a possibility of cation exchange between potassium and sodium (1.04%).

Table-1: Constituent Elements of PSB Compared to IMSB

Element	PSB (%)	IMSB (%)	Element	PSB (%)	IMSB (%)
C	8.25	6.25	P	1.13	-
N	30.87	25.50	S	1.32	0.57
O	55.64	56.10	K	1.80	-
Al	0.41	0.57	Na	0	1.04
Si	0.58	9.97			

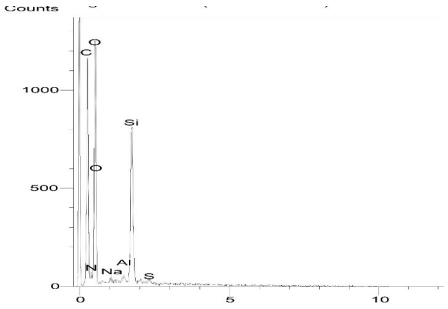

Fig.-1: EDX Spectra of IMSB

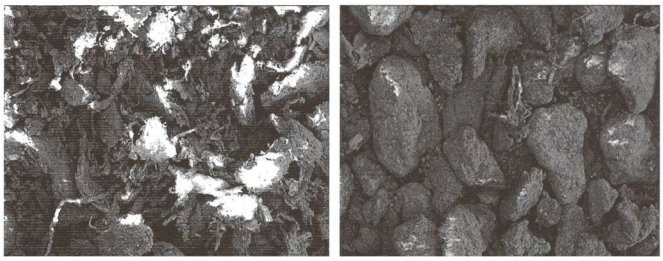

Fig.-2: SEM Images Showing the Surface Morphology of PSB (left) and IMSB (right)

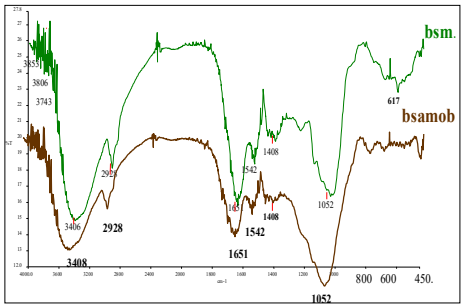

Fig.-3: IR Spectra of PSB (green) and IMSB (brown)

FTIR spectra of PSB and IMSB are shown in Fig.-4. FTIR spectroscopy spectra of PSB show absorption bands in the region of 3743 cm^{-1} showing O-H stretching (Si-OH), while in the region of 3406 cm^{-1} is O-H stretching (alcohol), asymmetric stretching -NH (primary amines and amides), and C-N stretching (amines).

The absorption band in the region of 2928 cm^{-1} shows O-H stretching (carboxylate) and C-H stretching (CH, CH_2, and CH_3 groups), while the region of 1651 cm^{-1} shows N-H bending (amine), C-O stretching (carboxylate), and C=O stretching (ketone, primary amide, and carboxylate). The absorption band observed in the region of 1542 cm^{-1} indicates NH and NH_2 bending (amide II band), C=O stretching (ketone, carboxylate, ester), C-O stretching (carboxylate), while in the 1408 cm^{-1} region indicates O-H bending, C-O-H bending (carboxylate), C=O and C-O (carboxylate), N-CO- (amide), CH_3 bending and CH_2 asymmetric bending, CH_3-S and CH_3-Si stretching. The absorption band in the area around 1250 cm^{-1} shows C-O stretching (carboxylic acid), while in the 1160 cm^{-1} region is C-O stretching (ether), C-N stretching, P=O stretching, and $–SO_3$ stretching. The absorption band at 1052 cm^{-1} indicates the presence of C-N stretching (aliphatic amine), -C-O stretching (primary alcohol, ether), O-C-C band (ester), Si-O-R stretching, P-OH stretching, P-O-C stretching and -C-O stretching (ester), while the bands at 700 and 617 cm^{-1} indicate out-of-plane NH swing (Amide II Band) and C-S stretching, respectively. In general, IMSB spectra are relatively unchanged compared to PSB spectra. Changes only occurred in the fingerprint area.[16]

Continuous Column Method

Effect of Adsorbate Flow Rate

When the metal cation solution is eluted into the working column packed with IMSB, there will be an interaction between the metal cation and the functional groups contained in the IMSB. The length of contact time will affect the quantitative interaction, so that it will affect the amount of metal ions adsorbed on the surface of the IMSB. Figure-4 shows the effect of the flow rate of the eluted solution for Cd^{2+} cations on the IMSB adsorption capacity. From the data, it can be seen that the optimum flow rate is around 0.5 mL/min. In theory, a greater flow rate means increasing the mass transfer of adsorbate, resulting in an increase in the adsorbed metals.[10]

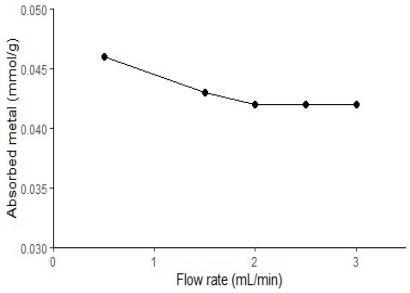

Fig.-4: Effect of Flow Rate on Biosorbent Capacity (mass 1.0 g, 25 mL of solution)

Effect of Initial pH of Metal Solution

The effect of initial pH of the solution on the absorption capacity of the biosorbent, which is IMSB, on Cd^{2+} cations, as summarized in Fig.-5. From the data, it can be seen that the absorption capacity of IMSB on each metal cation is greatly influenced by the initial pH of the solution. The characteristics of the effect of optimum pH on biosorption by IMSB changed slightly when compared to the characteristics of optimum pH on biosorption by PSB. The results showed that the absorption capacity of the biosorbent on Cd^{2+} cations was optimum at pH 4.0.

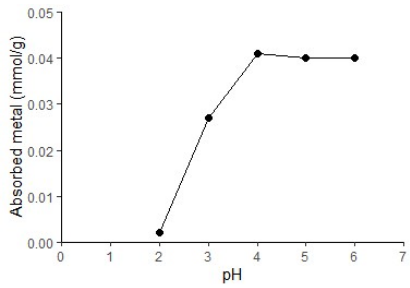

Fig.-5: Effect of Initial pH of Solution on the Absorption of Metal Cations by IMSB

Based on the characteristics of biosorption by IMSB packed in the working column, when associated with the nature of the metal and functional groups contained in the biosorbent, it is estimated that the interaction

between metal cations and biosorbents involves mechanisms, ion exchange, complexation, and electrostatic interactions. The functional groups of amine, amide, carboxyl and carbonyl as well as nitrogen and oxygen atoms in peptide bonds (amino), act as Lewis bases that can form coordinate covalent bonds with metal ions that act as Lewis's acids, while carboxylate groups at higher pH form carboxylate ions, so that they can interact electrostatically and ion exchange. At low pH, the surface of the biomass as a whole becomes positively charged, and the negative charge is reduced, due to protonation in functional groups, so that Cd^{2+} cations are relatively difficult to interact with the biomass.[11,12]

Effect of Metal Solution Concentration

The effect of metal cation concentration on the absorption capacity of IMSB and packed in the working column, on Cd^{2+} cations, as in Fig.-6. The data obtained shows that the amount of Cd^{2+} cations absorbed increases relatively sharply in proportion to the increasing concentration of the solution eluted through the column. The maximum biosorption of Cd^{2+} cations occurs at a concentration of around 250 mg/L (2.23mmol/L Cd^{2+}) with an absorption capacity of 5.90 mg (0.053 mmol) per gram of biomass.

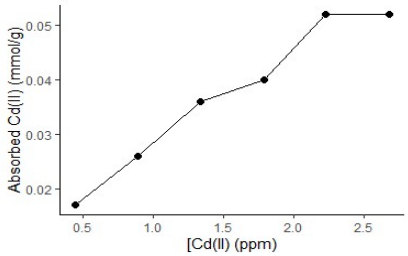

Fig.-6: The Effect of Metal Solution Concentration on IMSB Absorption

Effect of Immobilization in Sodium Silicate on Absorption Capacity

The effect of immobilization of S. subsalsa algae biomass on its absorption capacity of Cd^{2+} cations is shown in Fig.-7. In general, immobilization causes an increase in the absorption capacity of biosorbents. The increase in the absorption capacity of immobilized S. subsalsa algae biomass on sodium silicate of Cd^{2+} cations is 8.84%. This is due to silica immobilization provides mechanical strength to the algae.[13]

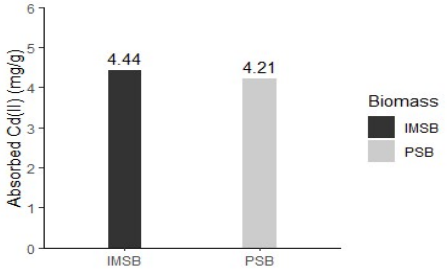

Fig.-7: Effect of immobilization on SS biomass

Effect of Eluting Acid Concentration on Regeneration of Columns

The optimum condition of HNO_3 solution as an eluent for the recovery of Cd^{2+} cations, Fig.-8. From the figure, it can be concluded that the recovery of Cd^{2+} cations is directly proportional to the concentration of nitric acid eluting the column with 0.5 M HNO_3 solution; the recovery results of Cd^{2+} cations are above 80%.

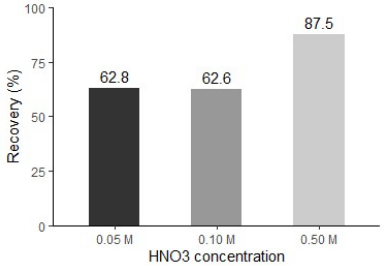

Fig.-8: Effect of Eluting Acid Concentration on IMSB Recovery

Application on Waste Sample and Concentration Factors

The application of the continuous method IMSB as a biosorbent on real samples, in the form of liquid waste containing Cd^{2+}, as shown in Fig.-9. The data on liquid waste samples for preconcentration purposes can be found in Table-6. It can be seen that IMSB gave a relatively high recovery percentage of 74.26%.

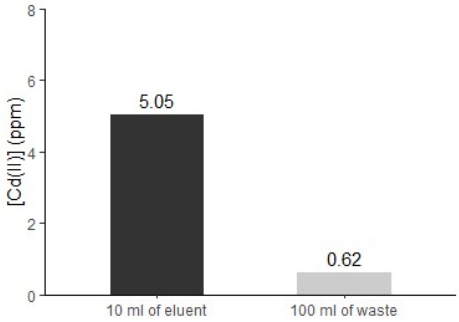

Fig.-9: Concentration of Cd(II) in liquid waste by IMSB

Table-6: Data on Liquid Waste Samples at Optimum Conditions for Preconcentration

	$[L]_{initial}$ (ppm)	$[L]_{eq}$ (ppm)	$[L]_{abs}$ (ppm)	$[L]_{conc}$ (ppm)	Recovery (%)
Cd(II)	0.68	0.06	0.62	5.05	74.26

CONCLUSION

Based on the research, it can be concluded that biomass immobilization causes an increase in biomass absorption capacity for Cd^{2+} cations by around 8.84%. The optimal number of the measured parameters are flow rate at 0.5 ml/min, pH 4, adsorbate concentration at 2.23 ppm with nitric acid concentration for recovery at 0.5 M. Recovery of Cd^{2+} cations is directly proportional to the eluting concentration nitric acid, where for Cd^{2+} cations column elution with 0.5 M HNO_3 solution the recovery results are above 80%. Application on a real waste sample resulted in a relatively high recovery of 74.26%. These results implied the usage of immobilized green algae biomass for the bioremediation of cadmium-polluted water.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-6:Clean Water and Sanitation*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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