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FUNDAMENTAL BEHAVIOR FOR BIOSORPTION OF DIVALENCE CATIONS *BY PLEUROTUS* MUSHROOM SPENT-SUBSTRATE

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ABSTRACT Biosorption behavior of *Pleurotus* mushroom spent-substrate was studied using two divalence cations: Ni(II) and Cu(II). Biosorption of both cations showed similar behavior on the effect of pH, initial concentration, temperature and contact time. Optimum biosorption was found to be between pH of 5-6, while lower initial concentration and temperature (as low as 10 $mg.L^{-1}$ and 5 ^oC), increased the biosorption efficiency. Rapid biosorption was observed to occur within 4-5 minutes of contact time. Therefore, metal removal using PMSS as the biosorbent needs to address the four fundamental parameters.

ABSTRAK Kelakuan biopenjerapan bagi substrat terpakai cendawan *Pleurotus* dikaji dengan menggunakan dua kation dua valensi iaitu Ni(II) dan Cu(II). Faktor pH, kepekatan awal larutan, suhu dan masa interaksi memberikan kesan yang sama terhadap kedua kation yang dikaji. pH 5-6 merupakan paras pengoptimuman biopenjerapan. Sementara itu, kepekatan awal larutan dan suhu yang rendah (serendah 10 $mg.L^{-1}$ dan 5 ^oC) telah meningkatkan kecekapan biopenjerapan. Kadar biopenjerapan maksima berlaku dalam tempoh masa bersentuhan selama 4-5 minit. Oleh itu, faktor pemboleh-ubah operasi penyingkiran logam dengan menggunakan PMSS sebagai bahan biopenjerap perlu mengambilkira empat kelakuan asas.

(**Keywords**: biosorption behavior, *Pleurotus sp.*, metal, mushroom spent-substrate)

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INTRODUCTION

Biosorption is an alternative method for metal removal. It is considered as a sustainable technology for being a passive, metabolic independent and metal-ion binding process that uses non-living biological materials. Recovery of metal ions from the biosorbent can be easily achieved by the use of diluted acid solution [1].

Recent studies on *Pleurotus* Mushroom Spent-Substrate (PMSS) for use as the green biosorbent for nickel (II) and copper (II) have been carried out [2, 3]. PMSS has shown the potential to be developed as a low environmental impact remediation technology. The two studies have shown four repetitive results that can be considered as fundamental behavior for the PMSS biosorbent. This study will highlight details of those behaviors.

MATERIALS AND METHODS

Preparation of Biosorbent and Metal Solutions

The same sample of PMSS [2,3] was used by sterilising it at 121 ^oC with 18 psi for 15 minutes and air-dried at the of temperature 60 ^oC. Dried sample of PMSS was ground into particle size of 710 µm and later rinsed with ultra pure water, twice to remove impurities. Finally, PMSS was again air dried at 60 ºC and stored in a desiccator.

For metal solutions, both were prepared by dissolving its salts in ultra pure water (resistance: 18.2 MΩ.cm). Analytical grade of copper (II) sulphate anhydrous ($CuSO_4$) and nickel (II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) salts (Merck, Germany) were used.

Experimental Set-Up for Biosorption Study

Fundamental behavior of PMSS biosorption was investigated with 0.7 g biosorbent in 50 mL of 50 mg.L^{-1} metal solution on an orbital shaker operating at 125 rpm and 60 minutes. Samples were later filtered and filtrates were analyzed with ICP-OES (7300DV, Perkin Elmer, USA). Behavior study included the testing of various initial pH range (from 1-6), initial metal concentration (10-250 mg.L^{-1}), temperature (5-35 ºC) and contact time (0.5-120 minutes). All experiments were conducted in duplicates.

Eq. 1 was used to measure metal biosorption efficiency for each selected operating variable in the experiment.

$$Percentage\ of\ heavy\ metals\ biosorption = \frac{(C_o - C_e)}{C_o}\ x\ 100\% \qquad \textbf{(Eq.1)}$$

C_o = initial concentration
C_e = final concentration

RESULTS AND DISCUSSION

Effect of pH

Metal biosorption by PMSS is a pH dependent process as shown in **Fig. 1**. Optimum biosorption was found to be in range of pH 5 to 6 with 43% to 48% efficiency for Cu (II) and Ni (II), respectively, of which were the un-adjusted initial pH. At lower pH condition, active binding sites of biosorbent are being protonated and charge repulsion formed. At the same time, metal ions have to compete with other protons to be bound with active binding sites on the surface of biosorbent. As a result, these circumstances reduced the biosorption efficiency. When the initial pH increase, the active binding sites of biosorbent deprotonate and increase the attraction between negative charge of biosorbent and positive charge of metal ions. Competition of metal ions with protons will become weaker and lead to a significant increase of the biosorption efficiency. For initial pH level more than 6, precipitation of metal has been observed. Owning to precipitation, the decrease of metal concentration in solutions limit the biosorption process, thus no observation was recorded. Similar findings by Babarinde *et al*. [4] and Asadi *et al*. [5] that have described that plant-based biosorbents showed similar trend of observation for Cu (II) and Ni (II) biosorption, respectively. It can be concluded that initial optimal pH plays a major role in biosorption process by influencing the active binding sites of biosorbent and the interaction with species of metal ions. Taking this into consideration, initial pH should be between pH 5 to 6.

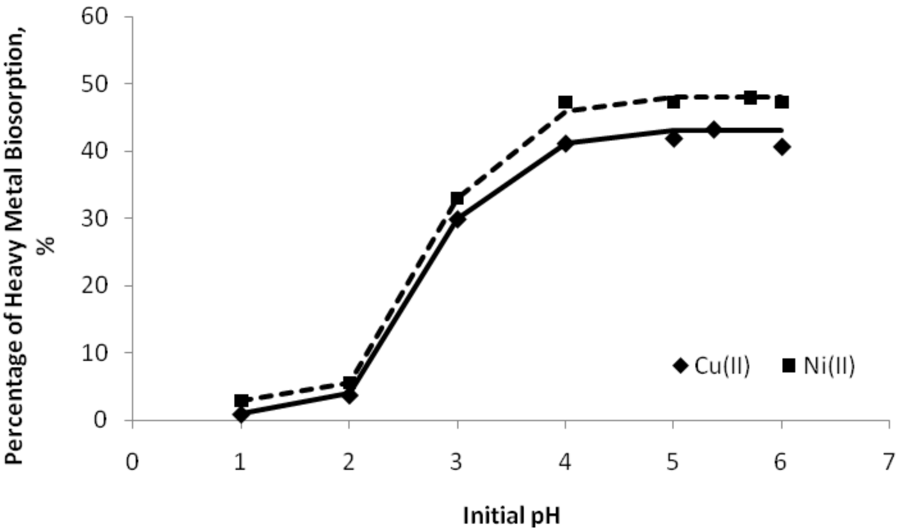

Figure 1. Effect of initial pH on Cu(II) and Ni(II) biosorption

Effect of Initial Concentration

Biosorption of metal decreased when initial concentration increased as shown in **Fig. 2**. In general, initial metal concentration acts as a driving force to overcome the mass resistance. Relatively the number of active binding sites in biosorbent decrease when initial metal concentration increase, thus leading to the reduction of biosorption efficiency. This result thus fall in-tandem with the rule of thumb for concentration gradient; the gradient between biosorbent and cation decrease when initial cation concentration increase, Similar results for biosorption of Cu(II) and Ni(II) by *Acacia* sawdust have been reported by Meena *et al*. [6] and tea-waste by Malkoc and Nuhoglu [7], respectively.

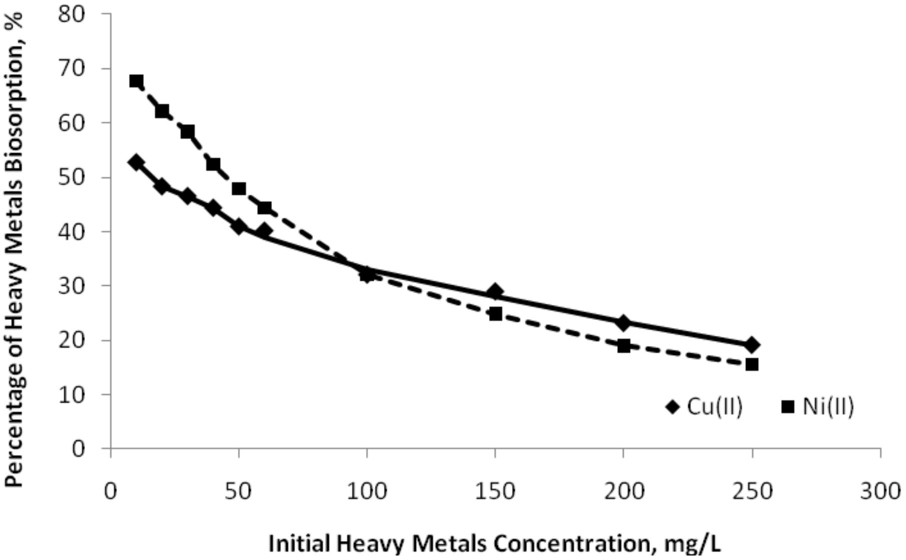

Fig. 2. Effect of initial concentration on Cu(II) and Ni(II) biosorption

Effect of Temperature

Fig. 3 shows effect of temperature on metal biosorption that was investigated at four different temperatures. When temperature increased from 5 ºC to 35 ºC, biosorption of Cu (II) and Ni (II) decreased from 44 % to 39% and 50 % to 47 %, respectively. This implied that the metal biosorption process of PMSS was an exothermic reaction in nature. Similar trend for temperature profile in this study have been reported by Arslanoglu *et al*. [8] with the use of esterified lemon as biosorbent. Increment of temperature has provided the driving force to overwhelm the mass transfer resistance; simultaneously increase diffusion rate of metal ions in external mass transport. Therefore, lower metal biosorption was observed due to high temperature in the surrounding which limits the sorption process.

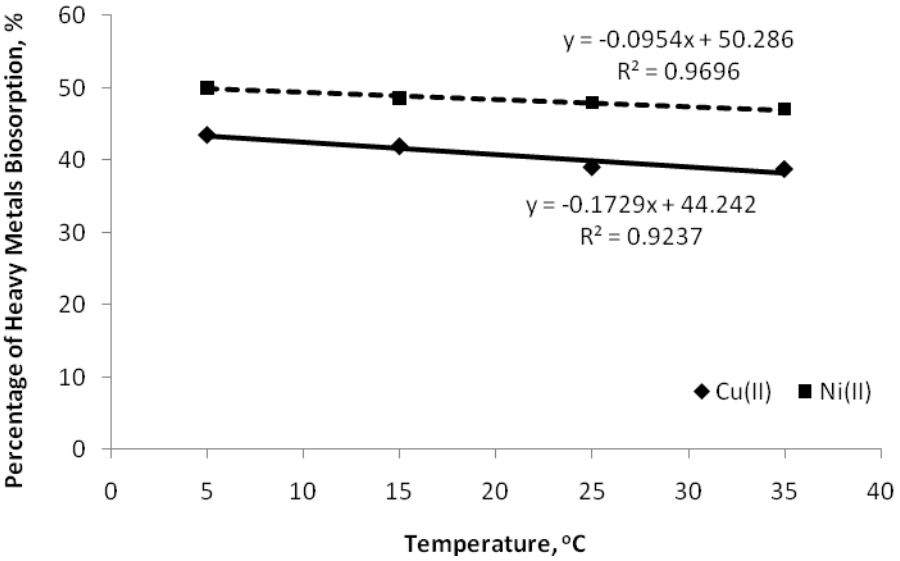

Fig. 3. Effect of temperature on Cu(II) and Ni(II) biosorption

Contact time

Referring to the contact time as shown in **Fig. 4**, the biosorption of metal is a two-phase process. The two-phase process can be observed within the 10 minutes of contact time; 40% and 45% of biosorption efficiency for Cu (II) and Ni (II), respectively. This indicates that the active binding sites of biosorbent are easily occupied by cation through rapid surface adsorption process withing three minutes and then followed by a gradual intracellular diffusion process. At the equilibrium stage, there is no changes of biosorption due to the saturation of available binding sites. Sangi *et al*. [9] and Kilic *et al*. [10] reported similar observation for Cu (II) biosorption when used tree leaves biosorbents. Similarly, studies for Ni (II) biosorption using cone and sawdust biosorbents also showed consistent results [11, 12]. This work shows that rapid superficial surface adsorption took place within 4-5minutes before it reached the next level of gradual intracellular diffusion process.

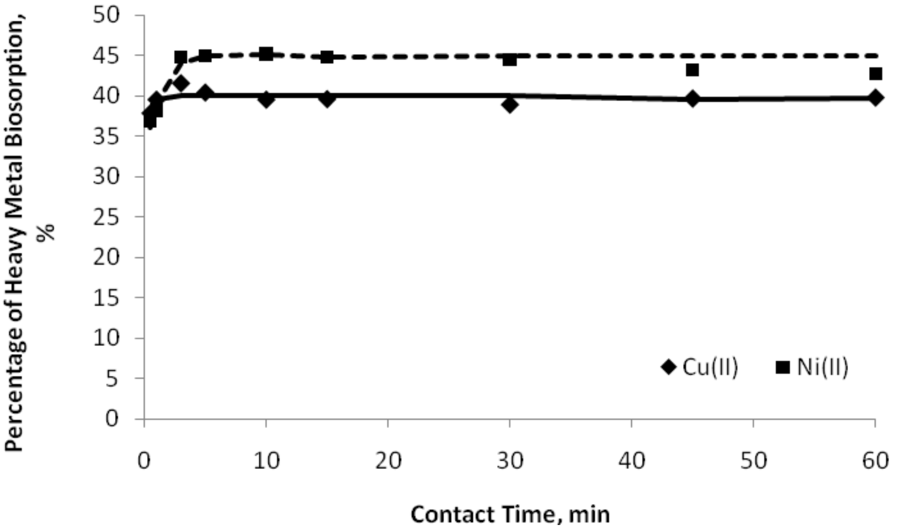

Fig. 4. Effect of contact time on Cu(II) and Ni(II) biosorption

CONCLUSION

The study has shown that for optimum biosorption of metals by PMSS, the process should be maintained at the higher side of acidity range which is between pH 5-6, with lower initial concentration. The biosorption process should address the mass transfer resistance due to the exothermic reaction by keeping control of temperature at a constant low level. The rapid surface adsorption takes place within 4-5 minutes of contact time, which is important for continuous flow wastewater treatment process.

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