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BIOMASS AS BIOSORBENT FOR MOLYBDENUM IONS

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ABSTRACT

Biosorbents have been focused as renewable materials of low cost, and have been used for metal removal from the wastewater by adsorption phenomenon. Biosorbents are prepared of biomass, whose reactive sites in its chemical structure have affinity to bind to metal ions. In this work, performance of corn husk, sugarcane bagasse, coir, banana peel, fish scale, chitin and chitosan as biosorbents of molybdenum(VI) ions in aqueous medium was evaluated. The adsorption experiments were investigated in a batch system varying the pH solution from 0.5 to 12 and the contact time between the phases from 2 min to 70 min. ^{99}Mo radioisotope was used as radioactive tracer for analysis of molybdenum ions by gamma spectroscopy using a HPGe detector. Results revealed that acidity of the solution favored the adsorption of Mo(VI) ions on the all biosorbents. Adsorption values higher than 85% were found on sugarcane bagasse, coir, corn husk, chitin and chitosan at pH 2.0. Only the chitosan was dissolved at pH 0.5 and a gel was formed. The models of pseudo-second order and external film diffusion described the kinetics of adsorption of Mo ions on the coir. This work showed that the studied biomass has high potential to be used as biosorbent of molybdenum ions from acidic wastewater, and the kinetics of Mo adsorption on the coir suggested high-affinity adsorption governed by chemisorption.

1. INTRODUCTION

Everyday, large amounts of heavy metals including molybdenum are discharged to the environment without an adequate treatment contaminating soils and waters. Those metals even at low concentrations cause damage to humans and to animals due to their high degree of toxicity. Biosorbents, low cost and renewable materials, have been investigated for metal removal from the wastewater by adsorption phenomenon [1]. Biosorbents are prepared from biomass, which have reactive sites in its chemical structure with affinity to bind to metal ions. In this work, performance of corn husks, sugar cane bagasse, coir, banana peel, fish scales, chitin and chitosan as biosorbents of molybdenum(VI) ions in aqueous medium was evaluated. The adsorption experiments were investigated in a batch system varying the pH solution from 0.5 to 12 and the time contacting between phases from 2 min to 70 min. ^{99}Mo radioisotope was used as radioactive tracer for analysis of molybdenum ions by gamma spectroscopy using a HPGe detector.

2. MATERIAL AND METHODS

Corn husk, coir (coconut shell), banana peel and sugarcane bagasse were cut and dried in sun. They were then chopped in a food processor, and sieved until obtaining of particle size ranging from 30 to 60 mesh. Scales of *Corvina* fish were washed several times with faucet water, sun-dried, triturated and sieved (30-42 mesh). Chitin and chitosan flakes were purchased from Merck or Sigma-Aldrich.

Nuclear Analytical Method. A radioactive tracer was used to quantify Mo ions in the solutions. The method consisted to add known activity of radioactive ^{99}Mo into solution of Mo ions. The ^{99}Mo presents the same chemical behavior of non-radioactive molybdenum, therefore it is possible to determine its concentration by gamma count. It is a fast method of analysis and provides reliable results. The ^{99}Mo tracer was supplied by the Centre of Radiopharmacy Centre – CR/IPEN.

The initial molybdenum solutions consisted of non-radioactive molybdenum in different concentrations containing the ^{99}Mo radioactive tracer and different pH values adjusted by the addition of drops of aqueous HCl or NaOH solutions.

2.1. Batch Adsorption

The adsorption of molybdenum on the each biosorbent was investigated in a batch system. All batch assays were conducted at 25 ± 2°C.

The initial molybdenum solutions (1.5 mL) were placed in contact with the each biosorbent (50 mg) contained in glass bottle at different time intervals under an agitation at 200 rpm. The supernatant solution was filtered through Whatman filter paper to separate the solid and liquid phases. The initial solution, which was not in contact with the adsorbent, was also filtered.

The activity of ^{99}Mo tracer of the supernatant solution was counted by a gamma ray spectrometer of HPGe (Canberra) before and after contact with the biosorbent.

The adsorbed percentage was monitored by analyzing the molybdenum concentration before and after contact with the biosorbent. The % removal was calculated from the Equation 1.

$$\% \text{ adsorbed} = (C_i - C_f) / C_i * 100 \qquad (1)$$

where C_i and C_f are the initial and final molybdenum concentration (mg L^{-1}) in the aqueous phase, before and after the contact of the aqueous phase with the biosorbent phase, respectively.

2.2. Effect of pH on Adsorption

By batch experiments, the influence of pH on adsorption was investigated in range from 0.5 to 12 with solutions de molybdenum concentration of 0.5 mg L^{-1}, and the contact time of 60 min. The pH value was measured using a pH meter at the beginning of the experiments and not controlled afterwards.

2.3. Effect of Contact Time

The batch experiments were conducted to quantify the effect of contact time on the molybdenum sorption. The contact time interval was from 2 to 70 min, and the solutions of molybdenum concentration of 25 and 100 mg L^{-1} at pH 2 were investigated.

3. RESULTS AND DISCUSSION

3.1. Effect of pH on Adsorption

The effect of pH on metal ions adsorption phenomenon is related to surface functional groups (active sites) present on the biosorbent and the metal ionic species in solution. The adsorption of a metallic ion on adsorbent can occur by physical adsorption when the weak Van der Waals forces originate from the interactions between electric dipoles of the metallic ion and the biosorbent. When the electronic structure of bonding ionic species is changed and these are bound to the surface of biosorbent by chemical bonds, as covalent or ionic bonds, the adsorption is known as chemical adsorption. Both phenomena can be simultaneous in the same reaction system.

The Mo ionic species in aqueous solutions depend on the molybdenum concentration and on the pH. In alkaline and neutral solutions molybdates are present as the monomeric $[MoO_4]^{2-}$ ion. As the pH is lowered polymerization condensation occurs, and various ionic species as dimolybdate, heptamolybdate, octamolybdate are formed according to Mo concentrations [2].

Fig. 1 shows the effect of pH on the adsorption of Mo ionic species on the biosorbents for Mo concentration of 0.5 mg L^{-1}. The Mo ionic species in each pH react differently with the active sites of the biosorbent and promote the variations on the adsorption process. Moreover, the active sites can also react with the solution medium. In lower pH, the surface charge may get positively charged and in higher pH the surface may get negatively charged which can increase or decrease the electrostatic forces of attraction. The adsorption phenomenon results the sum of these interactions.

As shown in Fig. 1, the solution pH affects the amount of Mo adsorbed. Adsorbed molybdenum amount (%) decreased when pH value increased. The Mo adsorption was better on the acidic pH than basic pH indicating that the polymerized ionic species are preferentially adsorbed on the biosorbents.

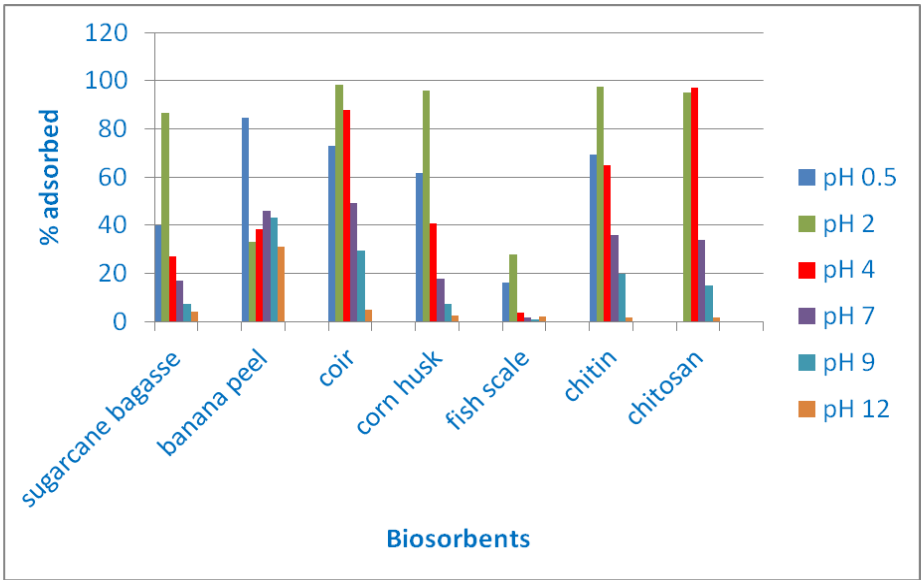

Figure 1: Effect of pH on the molybdenum adsorption on the biosorbents. [Mo] = 0.5 mg L^{-1}.

At pH 0.5, the expressive values of adsorption were observed on the banana peel, coir, corn husk and chitin that varied between 60% and 83%. The chitosan flakes were partially hydrolyzed and a chitosan gel was formed.

At pH 2, the adsorption was higher than 80% on the sugarcane bagasse, coir, corn husk, chitin and chitosan. The adsorption on the banana peel and fish scale was very low around 30%.

At pH 4 only coir, chitin and chitosan adsorbed more than 65%. At pH 7, 9 and 12, the adsorption decreased with the increasing of pH, and at pH 12 the adsorption was insignificant less on the banana biosorbent.

3.2. Effects of Contact Time and Initial Mo Ion Concentration

The coir was selected in order to investigate the effect of contact time on the Mo adsorption. Fig. 2 shows the percentage of adsorbed molybdenum on the coir for different contact times, where can be seen that the adsorption increased with increasing of contact time until to achieve a state of adsorption equilibrium. From this time, the adsorbed Mo amount on the coir is in equilibrium with the Mo concentration in the solution.

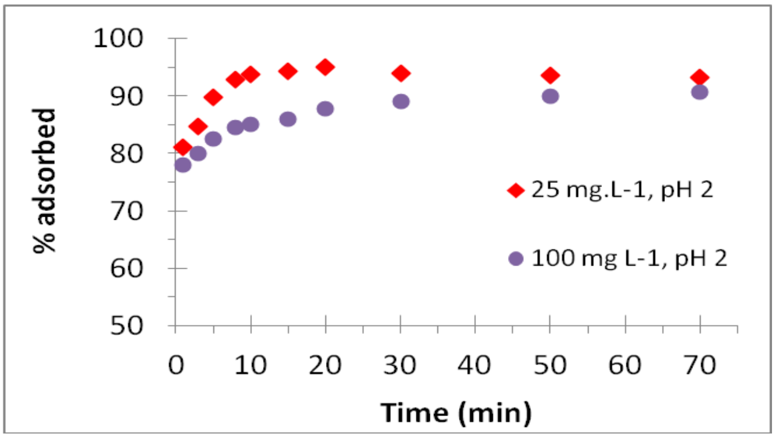

Figure 2: Effect of contact time on the Mo adsorption by the coir shell from the nitric solution, pH 2.

Fig. 3 shows the effect of initial concentration of Mo on adsorption kinetics of the coir. The data show that the initial Mo ion concentration influenced the equilibrium time and sorption capacity of the coir. The increase of the initial Mo concentration increased the contact time necessary to achieve equilibrium and increased the sorption capacity of the coir. The adsorption equilibrium time for 25 mg L^{-1} was achieved more rapidly than for 100 mg L^{-1}. For 25 mg L^{-1}, the equilibrium time was achieved in 10 min with adsorption capacity of about 0.9 mg g^{-1}, whereas, for 100 mg L^{-1} it was achieved in 30 min with the adsorption capacity of about 3.6 mg g^{-1}. The lower equilibrium time at the low concentration may be due to a reduced number of Mo ions for a large surface area of adsorption sites on the biosorbent, so all ions were readily adsorbed. At higher concentration there are more ions, and as the adsorption sites are occupied the adsorption becomes hard leading to a decrease in sorption rate, and the equilibrium time is achieved slowly and later on.

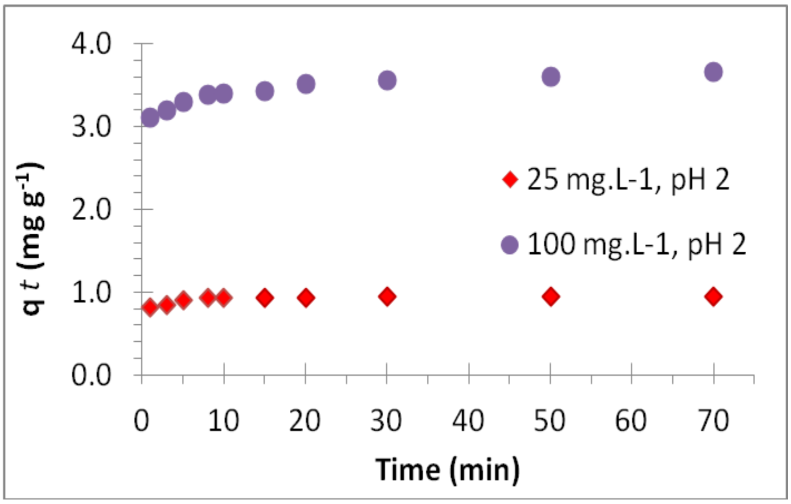

Figure 3: Sorption capacity of the coir for Mo ion species from the nitric solution, pH 2.

3.2. Kinetics

Three kinetic models were applied to experimental data in order to investigate the mechanism of sorption phenomenon of Mo ions on coir, the pseudo-first order (Eq. 2), pseudo-second order (Eq. 3) and intraparticle diffusion (Eq. 4) models.

$$\log(q_e - q_t) = \log(q_e) - (k_1/2.303)\, t \quad . \tag{2}$$

$$t/q_t = 1/(k_2 q_e^2) + (1/q_e)\, t \; . \tag{3}$$

$$q_t = k_{id}\, t^{1/2} + C \qquad . \tag{4}$$

where q_e and q_t (mg g^{-1}) are the amount of adsorbed Mo (or the sorption capacity) at equilibrium and at time t (min), respectively; k_1 (min^{-1}) is the rate constant of pseudo-first order sorption and k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second order kinetics. The Eq. 2 and 3 are the integrated form and linearized form of the models. If pseudo-first and pseudo-second order kinetics are applicable, their respective plots should give a linear relationship, and the kinetics parameters can be determined from the slope and intercept of plot [3].

For intraparticle diffusion model, k_{id} (mg g^{-1} min^{-1}) is the intraparticle diffusion rate constant and C is the intercept. According to Eq. 4, a plot of q_t versus $t^{1/2}$ should be a straight line with a slope k_{id} and an intercept C when adsorption mechanism follows the intraparticle diffusion process. If the straight line passes the origin, intraparticle diffusion is the rate controlling step. Otherwise, the adsorption process may involve some other mechanisms along with the intraparticle diffusion. [4].

In order to analyze the pseudo-first order, eq. 2, the equilibrium sorption capacity, q_e, must be known. In most cases, q_e is unknown and often it has been found by extrapolating the experimental data to $t = \infty$.

In this study, the values of q_e were found by means of extrapolating of the plot of q_t against t to $t = \infty$, according Fig. 3. The values of q_e were found to be equal 0.951 mg g^{-1} and 3.665 mg g^{-1} for initial concentration of 25 mg L^{-1} and of 100 mg L^{-1}, respectively.

Fig. 4 and 5 show the linear relationship of plots of pseudo-first order and pseudo-second order models, from which the kinetics parameters were determined from slope and intercept of the plots and are summarized in Table 1. Fig. 4 shows that linear relationship of pseudo-first order is not well represented for the experimental data although the correlation coefficients are relatively close to one unity. Furthermore, the value of calculated q_e are so far distant from the values of extrapolated q_e, so, the experimental results did not follow pseudo-first order to describe the adsorption kinetics of Mo(VI) ions on the coir.

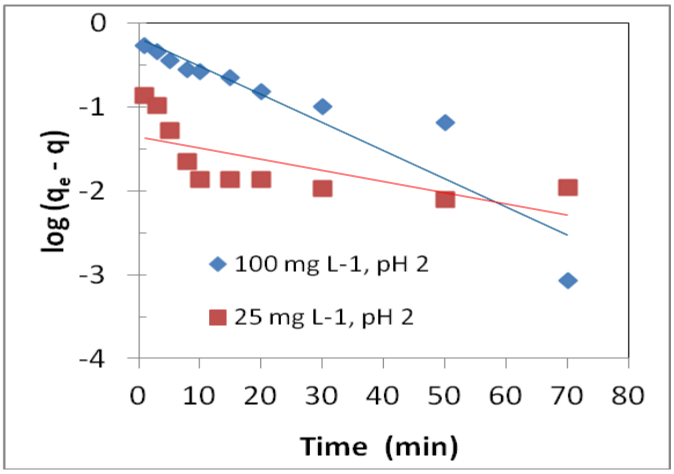

Figure 4: Pseudo-first order sorption kinetics of Mo onto coir.

The pseudo-second order kinetic model fitted well the experimental data as can be observed in Fig.5, confirming the correlation coefficients higher than 0.999. The values of calculated q_e were similar to the extrapolated q_e, indicating that pseudo-second order is more suitable for interpreting the kinetic data of the Mo adsorption process on the coir. Also, it was found that the rate constant (k_2) decreased as the initial concentration of Mo increased confirming the increase of the time equilibrium to higher Mo concentration.

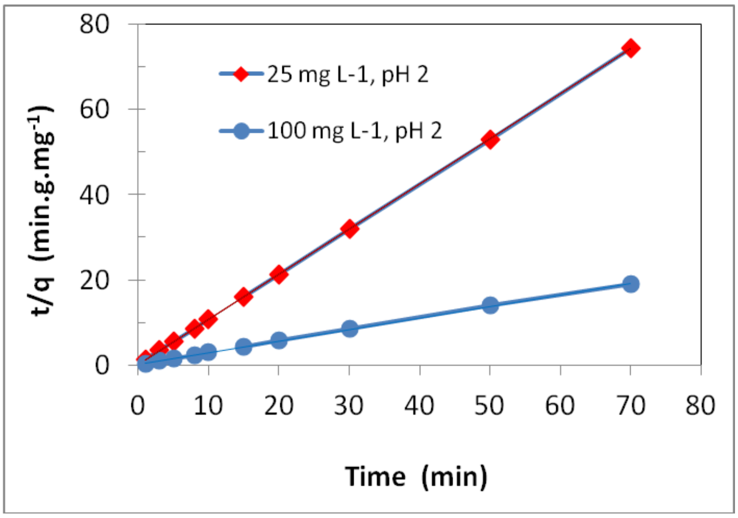

Figure 5: Pseudo-second order sorption kinetics of Mo ionic species onto coir from of pH 2 solution.

According to the pseudo-second order, this suggests that this sorption system based on the assumption that the rate-limiting step may be chemical sorption or chemisorptions [5] involving valence forces through sharing or exchanging electrons between Mo ions and activating sites of coir.

The coir possesses low porosity and therefore this suggests that the adsorption process involves only external active surface of biosorbent. On the other hand, it is known that the diffusivity of adsorbate plays an important role in determining the overall adsorption rate, and the pseudo-second order is not enough to predict the diffusion mechanism.

There are two main types of diffusion processes, film diffusion and intraparticle diffusion, which can be investigated by Weber *et al.*, eq. 4 [6]. From the Fig. 6, that shows the plots q_t versus $t^{0.5}$ for Mo ions on the coir, it was observed that the adsorption process tends to be followed by two phases and the lines have nonzero intercept. This reveals that intraparticle diffusion is not rate controlling step. On the other hand this reveals also the existence of external film diffusion during the adsorption process.

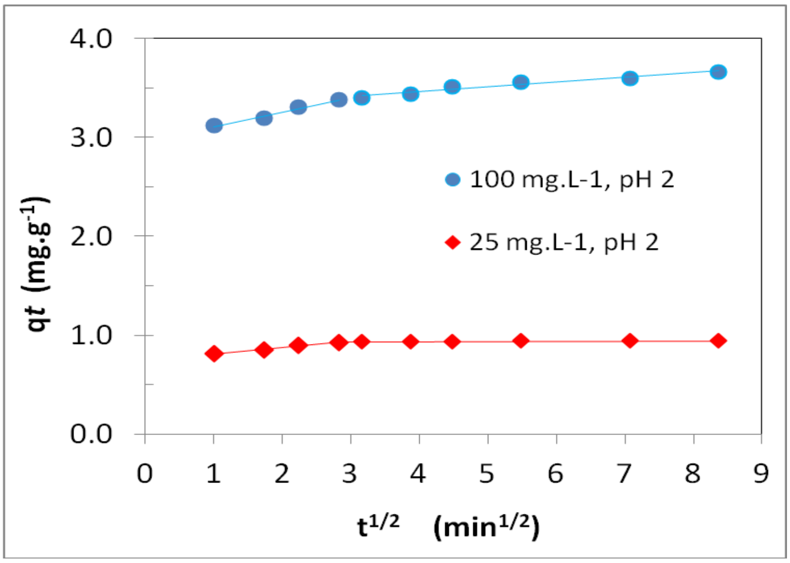

Figure 6: Intraparticle diffusion kinetics of Mo ionic species onto coir from of pH 2 solution.

The plots show two linear sections in which the value of $k_{i,1}$ is much higher than $k_{i,2}$, and it increased with the increasing initial Mo concentration (Table 1). Higher values of K_{id} illustrate an enhancement in the rate of adsorption. The first linear section showed good linearity to the data. This can indicate that the initial adsorption may be dominated by the film diffusion process probably due to the low porosity of coir. For the adsorption at higher Mo concentration, the existence of second straight line with good linearity to the data may be due to the rearrangement of the Mo ions which were initially adsorbed on the coir [7].

Table 1: Kinetic parameters for adsorption of Mo (VI) ions on coir at room temperature from nitric solution, pH 2

Initial concentration	**25 mg L^{-1}**	**100 mg L^{-1}**
	Pseudo-first order	
k_1(min^{-1})	**0.228**	**0.077**
q_e, extrapolated (mg g^{-1})	**0.951**	**3.665**
q_e, calculated (mg g^{-1})	**0.165**	**0.668**
r^2	**0.964**	**0.864**
	Pseudo-second order	
k_2 (g mg^{-1} min^{-1})	**20.678**	**0.404**
q_e, calculated (mg g^{-1})	**0.937**	**3.674**
r^2	**0.9999**	**0.9998**
	Intraparticle diffusion	
$K_{id\ 1}$ (mg g^{-1} min^{-1})	**0.013**	**0.148**
C_1 (mg g^{-1})	**0.860**	**2.961**
r_1^2	**0.979**	**0.986**
$K_{id\ 2}$ (mg g^{-1} min^{-1})	**0.002**	**0.048**
C_2 (mg g^{-1})	**0.929**	**3.268**
r_2^2	**0.527**	**0.947**

4. CONCLUSIONS

Results indicated that the acidity of the solution favored the Mo adsorption on the biosorbents. Adsorption values higher than 85% were found at pH 2.0 for sugarcane bagasse, coir, corn husk, chitin and chitosan. Although at pH 0.5, very acidic, the Mo adsorption on the biosorbents decreased, except for banana peel. Only the banana peel biosorbent adsorbed more than 80% at pH 0.5. Chitosan biosorbent was hydrolyzed and a gel was formed at pH 0.5. From the solutions of basic pH, the adsorption values were lower than 45%. Among the studied kinetics models, the pseudo-second order and external film diffusion described the adsorption mechanism of Mo ions on the coir. Between the two models, the pseudo-second order described better the adsorption behavior over the whole range of studies and predicts that the adsorption mechanism is in agreement with chemisorptions being the rate controlling step. This work showed that the studied biomass has high potential to be used as biosorbent of molybdenum ions from acidic wastewater, and the kinetics of Mo adsorption on the coir suggested high-affinity adsorption governed by chemisorption.

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