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Biosorption of Pb(II) and Fe(III) from aqueous co-solutions using chemically pretreated oil palm frond

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Abstract

The removal of Pb(II) and Fe(III) from aqueous solutions using specially pretreated oil palm frond (OPF) as biosorbents was investigated. OPF biosorbents were prepared through four different pretreatment processes; SCM0.5 (0.5M NaCl/0.5M Na_2SO_4 solution 1:1), SM1 (1M Na_2SO_4 solution), CM1 (1M NaCl solution) and SMCM1 (SM1 and CM1 1:1). The biosorbents were characterized using scanning electron microscope and energy-dispersive X-ray spectroscope. Variables such as adsorbent dosage (0.25 g/L to 1.75 g/L) and agitation time (10 min to 80 min) were investigated. The pH range for the solutions was adjusted between 5 and 6. The optimum biosorbent dosage and agitation time for removing Pb(II) and Fe(III) using the SCM0.5 biosorbent were 1.25 g/L and 20 min, respectively. Compared with the other biosorbents, SCM0.5 exhibited the highest adsorption efficiency of 98% and 92% for Pb(II) and Fe(III), respectively. Adsorption equilibrium data were fitted into three adsorption isotherm models for the SCM0.5 and SMCM1 biosorbents. The Langmuir isotherm accurately fits the results for Fe(III) ions, whereas the Freundlich isotherm shows the best result for Pb(II). Kinetics of the biosorption process via the SCM0.5 and SMCM1 biosorbents were analyzed using pseudo-first-order and pseudo-second-order models. The latter demonstrates better fit for both metals.

Key words: Biosorption; Pb(II) ; Fe(III) ; oil palm frond; pre-treatment; kinetic model

1. Introduction

Industrial effluents are the main contributors to heavy metal contamination of water resources. Toxic heavy metals can typically enter the food chain through the contamination of natural bodies of water. These contaminants can be toxic even at extremely low concentrations and can pose a serious threat to the environment and human health. [1, 2]

Common techniques used to remove heavy metal and dye from effluents include ion exchange [3], adsorption [4], chemical precipitation [5], reverse osmosis [6], and solvent extraction. [7] Adsorption is one of the most promising technologies because its cost-effectiveness, low by product formation, and simplicity to operate while causing no secondary pollution. [8-10] Adsorption process has been of interest as an effective, environmental friendly and economical method due to its high efficiency, low cost and easy operation. [11] The removal of dyes and metal ions from the solutions can also be achieved through physico-chemical interactions between biomass and aqueous metal solution. This process is commonly known as biosorption. Although activated carbon is a common adsorbent for the removal of organic and inorganic compounds, biosorbents have been used to improve the effectiveness of heavy metal adsorption even at extremely low pollutant concentration. [12] Biosorbents refer to adsorbents from dead biomass as well as living plants and bacteria with high similarity and sorption capacity. [13] The adsorption process can be affected by some process parameters such as pH, initial concentration, dosage of adsorbent and contact time. [14, 15]

Biosorbents have been modified to increase their active binding sites making them highly effective for sorption. [16] The selectivity of heavy metal removal depends on the type of available functional groups in the biosorbents, which can be varied through different biosorbent modification processes. Southichak et al. [17] used pretreated reed as the biosorbent to remove Pb(II). The biosorbent was pretreated separately with neutral salts ($CaCl_2$, NaCl, KCl, and $MgCl_2$) and basic salts [$Ca(OH)_2$, NaOH, KOH, $Mg(OH)_2$, and $Ba(OH)_2$] to possibly enhance its adsorption capacity. The amounts of Pb(II) adsorbed onto the reed pretreated with basic salts were relatively higher than those adsorbed onto the reed pretreated with neutral salts. Among the biosorbents, the reed biomass pretreated with NaOH, which removed 51.4% of Pb(II), was the most effective one. Qi and Aldrich [18] used HCl-pretreated tobacco dust to adsorb Pb(II), Cu(II), Cd(II), Zn(II), and Ni(II) from aqueous solutions and approximately 90% Pb(II) removal was achieved under the optimum conditions. Short hemp fibers were used after pretreatment with 17.5% NaOH and 0.7% $NaClO_2$ to remove Pb(II), Cd(II), and Zn(II). Rapid biosorption was observed wherein approximately over 80% of the total uptake capacity of metal ions was achieved. [19] Spent mushroom was also used as a biosorbent after modification with dodecyl dimethyl benzyl ammonium bromide to remove Cr(VI). 80% of the heavy metal was removed under the optimum conditions. [20] Xie et al. [21] prepared magnesium chloride-modified *Lentinula edodes* (MMLE) by treating the biomass with a mixture of NaOH, ethanol and $MgCl_2$ for adsorption of Cd(II) and Cu(II). 95% and 96% of Cd(II) and Cu(II) were removed under the optimum conditions, respectively.

Reports on the selective removal of Fe(III) and Pb(II) using agricultural waste materials such as oil palm biomass are rarely found in literature. Thus, this investigation on the use of oil palm biomass in removing heavy metal ions from aqueous solutions is timely. Pretreatment of biosorbent using different chemical reagents in order to improve the biosorbption efficiency have been reported in literature. [22-24] The fact that the biosorption process can be further improved by applying selective pretreatments based on heavy metals existing in the solution justifies further works in this area.

The present study aims to investigate the potential of selective-pretreated oil palm frond (OPF) as biomass for adsorbing Fe(III) and Pb(II) ions from aqueous solutions. Selective pretreatments have been performed using NaCl and Na_2SO_4 in different ratios to remove Fe(III) and Pb(II), respectively. The biosorbents have also been characterized to determine their physical and chemical characteristics that can affect the biosorption process. Effects of adsorbent dosage, contact time and initial ions concentration on heavy metals removal from aqueous solutions have been particularly investigated. Adsorption equilibrium data have been analyzed using different adsorption isotherm models, and the adsorption kinetics of the two metals have been performed.

2. Methodology

2.1. Biomass preparation

OPF was obtained from an oil palm plantation in Nibong Tebal, Penang, Malaysia. The frond was thoroughly washed in boiling distilled water to remove impurities. Then, it was dried in an oven for 24 h at 110 °C, ground, and sieved with a mesh size of 200 μm. Prior to the adsorption experiments, several chemical pretreatments were performed on the pulverized sample to prepare the following biosorbents: SM1 (with 1.0 M Na_2SO_4 for 24 h), CM1 (with 1.0 M NaCl for 24 h), and SCM0.5 (with 0.5 M Na_2SO_4 and 0.5 M NaCl in 1:1 liquor ratio for 24 h). All samples were filtered and thoroughly washed with distilled water. The samples were then dried in an oven for 24 h at 95 °C. SMCM1 was prepared by mixing SM1 and CM1 at a weight ratio of 1:1. The chemically pretreated samples, with their respective biosorbent preparation conditions are presented in Table 1.

2.2. Biomass characterization

A scanning electron microscope (SEM) (Leo Supra 50 VP field emission) was used to characterize the morphological characteristics of the biosorbents. Energy-dispersive X-ray spectroscopy (EDX) analysis was conducted to determine the elemental composition of the pretreated biomasses.

2.3. Preparation of metal solution

Synthetic wastewater solutions containing Fe(III) and Pb(II) were prepared by dissolving analytical grade $FeCl_3$ (R&M Chemicals, 99 %) and $Pb(NO_3)_2$ (Avonchem Ltd, 99 %) in deionized water. The concentration of each metal in the solution was fixed at 500 mg/L. Sodium hydroxide (1.0 M) and hydrochloric acid (1.0 M) solutions were used for pH adjustment of the synthetic wastewater solution.

2.4. Biosorption test

Batch adsorption tests were conducted by mixing the biosorbents with 100 mL of the solutions containing known metal ion concentrations. The pH of the solutions was adjusted between 5 and 6 [25] to achieve optimum biosorption. Biosorption experiments were conducted to particularly determine the effects of adsorbent dosage (0.25, 0.50, 0.75, 1.00, 1.25, 1.50, and 1.75 g/L) and agitation time (10, 20, 40, 60, and 80 min). The effects of initial concentration of metals in the solution were investigated with one metal concentration fixed at 40 mg/L and other one was varied between 10 and 100 mg/L. At the end of each experiment, the mixtures were filtered, and the filtrates were analyzed for metal ion concentration. A blank solution was also tested for each experiment to determine the exact amount of heavy metal biosorption by excluding the effect of heavy metal precipitation. The percentage of heavy metal removal from the solution is calculated as follows:

$$\%\ \text{Removal}=\frac{C_0\text{-}C_i}{C_0}\times 100\ \% \qquad (1)$$

Where, C_0 is the initial concentration while C_i is the final concentration of the heavy metals. Isotherm studies were performed by varying the initial metal ion concentration in the solution (10, 20, 40, 60, 80 and 100 mg/L for each salt). Based on the mass balance relationship, the adsorption capacity q_e (mg/g) is calculated as follows:

$$q_e=\left(C_0\text{-}C_i\right)\frac{V}{W} \qquad (2)$$

Where, V is the volume of the solution (L) and W is the mass of the biosorbent (g). Triplicate runs were performed to all these experiments to increase the accuracy of the data. At the end of each run, the sample was filtered rapidly, and the metal concentration in the filtrate was determined using an atomic absorption spectrometer (AAnalyst 100, Perkin Elmer).

3. Results and discussion

3.1. Biosorbents characterization

The results of SEM and EDX analyses of the biosorbents before and after the biosorption of heavy metals in the solutions are shown in Figs 1 and 2, respectively. An evident morphological difference was observed on the surface of the biosorbents before and after the biosorption of metals. The micrographs also show that the biosorption process caused some changes on the surface texture of the biosorbents. The surfaces visibly became smoother after biosorption. Sharp edges, which were the most fragile portions of the biomass particles, were partially eliminated after biosorption. The binding of heavy metals to the cell walls could proceed through a two-step mechanism. First, the metals will interact with the reactive chemical groups in the biosorbent, and second, the same interaction sites create a condition on the surface of the biomass wherein additional removal of heavy metals can occur via surface precipitation. All characteristics of the biomass suggested that some physical changes could have occurred after biosorption. The surface of metalloaded cells appeared vague and distorted as well as partially damaged by the heavy metal ions.

Figs 1(a) and 1(b) show the SEM images of the SM1 biosorbent before and after the adsorption of heavy metals, respectively. As shown in Fig 1(b), the surface structure of SM1 changed significantly, with the number of pores reduced drastically after biosorption. This change was mainly attributed to the adsorption of Pb(II) and Fe(III) ions on the surface of the biosorbent. The EDX spectra of SM1 before and after adsorption are presented in Figs 2(a) and 2(b), respectively. The EDX results confirmed that the dense electron area on the surface of SM1 was mostly caused by Pb ions. A relatively lower amount of Fe ions was observed in the EDX image of SM1. The EDX analysis concluded the presence of Pb(II) and Fe(III) bands, and the deficiency of Na. This could be indicative of ionic exchange mechanism between sodium that was mostly substituted by Pb(II) and lower amount of Fe(III) on the surface of the biosorbents. According to Greenwood and Earnshaw, sodium sulfate is a typical ionic sulfate containing Na^+ and SO_4^{2-} ions. The existence of sulfate in the solution is indicated by the easy formation of insoluble sulfates when Pb^{2+} ions are available in the solution. [26]

Figs 1(c) and 1(d) show the SEM photographs of the CM1 biosorbent before and after adsorption, respectively. The surface morphology of CM1 shows that most of the surface area is covered by Fe(III) and only a few particles of Pb(II) are spotted on the surface. The EDX spectrum of CM1 also confirmed the higher uptake of Fe(III) and small peak of Pb(II). The biosorption of metals might be due to the presence of Chlorine group that can bind metal ions, suggesting the interaction between metals with chlorine functional groups in CM1. The appearance and disappearance of Na^+ peaks in EDX spectrum in CM1 before and after biosorption process indicate that the process also included ion-exchange mechanism for the removal of both metal ions by CM1. According to Ebbing et al., sodium chloride could perform as ion-exchanger in the presence of Fe^{3+}. [27]

The SEM photographs of SCM0.5 before and after adsorption are provided in Figs 1(e) and 1(f), respectively. Pores are observed on the surface of SCM0.5 before adsorption, which are considered beneficial for improving mass transfer of metal ions. As shown in Fig 1(f), the surface of SCM0.5 is covered by Fe(III) and Pb(II), but some available pores remain visible on the surface texture. The EDX spectra of SCM0.5 before and after adsorption are presented in Figs 2(e) and 2(f), respectively. The spectra indicate that SCM0.5 had the highest adsorption for both Fe(III) and Pb(II). The results of the EDX analyses showed the presence of Na, Cl, O, S, and C as detectable species in SCM0.5. The presence of these elements could influence the adsorption mechanism through ionic exchange interactions.[28]

The SEM images of SMCM1 before and after adsorption are presented in Figs 1(g) and 1(h), respectively. The micrographs show that significant changes occurred after adsorption on the surface texture of the SMCM1 biosorbent. The EDX spectra of SMCM1 before and after adsorption are provided in Figs 2(a) and 2(b), respectively. The EDX results clearly show the presence of Pb(II) and Fe(III) bands. Moreover, the SMCM1 biosorbent exhibited lower adsorption of heavy metal ions compared to SCM0.5. Therefore, the differences in Fe(III) and Pb(II) biosorption could be ascribed to the varying affinities of each metal to the functional groups in the biosorbents.[29, 30]

In summary, the superior performance of the SCM0.5 in the biosorption process indicated that the pretreatment of biomass by both NaCl and Na_2SO_4 could improve the biosorption process by generating ionic exchange interactions. SCM0.5 and SMCM1 were more useful biomasses for removal of Pb(II) and Fe(III) to improve the biosorption efficiency and the removal mechanism is as shown in Scheme 1.

3.2. Effect of biomass dosage

The effects of adsorbent dosage on Pb(II) and Fe(III) removals are illustrated in Figs 3(a) and 3(b), respectively. Here, the concentration of each metal in the solution was fixed at 500 mg/L. Removals of Pb(II) and Fe(III) were enhanced as the amount of biosorbent was increased from 0.25 g/L to 1 g/L for the CM1 and SM1 biosorbents. The metal removal trend became nearly constant after a biosorbent dosage of 1 g/L. The available metal ions were insufficient to cover all exchangeable sites on the biosorbent at high sorbent dosages with a fixed initial concentration of heavy metals. The increase in unsaturated adsorption sites throughout the adsorption process was responsible for the low metal uptake and a decrease in adsorption capacity.

Fig 3(a) indicates that SM1 biosorbent exhibited significant potential for adsorbing up to 80% of Pb(II), whereas the CM1 biosorbent could only adsorb up to 25% of Pb(II) at a dosage of 1 g/L. Meanwhile, Fig 3(b) shows that up to 74% of Fe(III) was removed using the CM1 biosorbent while SM1 biosorbent could only remove a maximum of 15% of Fe(III).

Biosorption selectivity could be attributed to the component used in the pretreatment process. Biosorption can happen through the coordination of metals with surface functional groups, such as sulfates and chlorides. SM1 biosorbent was treated with a sulfate functional group, which would preferably adsorb Pb ions, [26] whereas CM1 biosorbent was treated with a chloride functional group, which could adsorb Fe ions.

In general, SMCM1 and SCM0.5 biosorbents exhibited similar adsorption behavior. However, SCM0.5 presented the highest removal levels for both metal ions. Among the pretreated biosorbents, SCM0.5 demonstrated the highest metal removal efficiency, adsorbing 98% and 92% of Pb and Fe ions, respectively from the solutions at an adsorbent dosage of 1.25 g/L. With the increase in the amount of functional groups, SCM0.5 demonstrated better results in improving cation exchange capacity for the biosorption.

Removal efficiency was enhanced with increasing adsorbent dosage for any given initial metal concentration. Increasing adsorbent dosage provided greater surface area for the adsorption and exchange of ions. [31] Furthermore, adsorption could be attributed to the binding of metal ions onto the surface functional groups (such as chlorides and sulfates) that were present on the biosorbent. [32]

Among previously reported biosorbents, SCM0.5 exhibited higher heavy metal removal efficiency. Obuseng et al. [33] reported that 8.33 g/L *Moringa oleifera* seeds could remove 82% of Pb(II) in 60 min, whereas 1.25 g/L SCM0.5 could remove 99% Pb(II) in 20 min. For further comparison, Lasheen et al. [34] employed a modified orange peel biosorbent to remove Pb(II). After 30 min of treatment using 4 g/L of the prepared biosorbent, 99% Pb(II) removal was achieved.

3.3. Effect of contact time

Effects of contact time on the adsorption of Pb(II) and Fe(III) are shown in Figs 4(a) and 4(b), respectively. Rapid rates of adsorption are noted during the first 20 min of sorbate–sorbent contact for both heavy metals. The rate of heavy metal removal could be generally characterized as follows: (a) a rapid initial uptake, (b) a decreasing rate of adsorption, and (c) a nearly insignificant adsorption rate after 20 min for SCM0.5 and SMCM1, and after 40 min for SM1 and CM1.

As noted in Fig 4, SCM0.5 and SMCM1 exhibited very similar behaviors under the same reaction conditions with slightly higher removal rates of both Pb(II) and Fe(III) for SCM0.5. When SCM0.5 was used as the biosorbent, 99% and 92% of removals were observed after 20 min for Pb(II) and Fe(III), respectively. Meanwhile, the maximum removal rates of Pb(II) and Fe(III) by SM1 after 40 min of reaction were 79% and 17%, respectively. In addition, CM1 achieved the highest removal rates of 25% and 74% for Pb(II) and Fe(III), respectively. These findings suggested that SM1 and CM1 were, in fact, unsuitable biosorbents for Fe(III) and Pb(II), respectively, which could be attributed to the component used in the pretreatment process as discussed in Section 3.1.

The results also revealed that metal removal as a function of contact time occurs in two steps. The first step involves a rapid metal uptake within the first 20 min of contact time. The second step is characterized by the subsequent slower removal rates of metal. Rapid adsorption during the initial stage of the process was attributed to the larger surface area that was available for the biosorption of metal ions. [35] However, the exhaustion of biosorption sites during the process resulted in lower adsorption rates during the second stage. [30, 32 36] Similarly, a high percentage of heavy metal removal was reported with a high biosorbent dosage and long contact time. Ramana et al. [32] reported that 6 g/L pigeon pea hulls could remove 98.5% of Pb(II) in 50 min while Zhu [37] reported that 2 g/L functionalized silica spheres in pH 7 and 60 min could adsorb 82.65% of Pb(II) from aqueous solutions. Meanwhile, based on the results of the current study, 1.25 g/L SCM0.5 could remove 99% of Pb(II) in 20 min.

3.4. Effect of initial metals concentration

Effects of initial metal concentration on the adsorption of Pb(II) and Fe(III) by SCM0.5 and SMCM1 are illustrated in Figs 5(a) and 5(b), respectively. It is shown that the total removal percentage of Pb(II) and Fe(III) decreased by increasing the initial concentration while the removals of both heavy metals with SCM0.5 were higher as compared to those of SMCM1. The amount of Pb(II) adsorbed on SCM0.5 decreased from 94% to 84% as the initial concentration of Fe(III) was increased from 10 to 100 mg/L while, the amount of Fe(III) adsorbed with fixed amount of Pb(II) decreased from 91% to 77%. It was also observed that the amount of Pb(II) and Fe(III) adsorbed per unit mass of biosorbent increased with the increase in the initial metal concentration. The increase in the initial concentration increased the sorption capacity of both heavy metals for both SMCM1 and SCM0.5.

The initial concentration of heavy metals plays a major role in biosorbetion efficiency. The biosorption can easily reach equilibrium when the initial concentration was low due to available active sites on the surface of biosorbent. The available sites decreased by increasing the initial concentration and the surface of biomass could become saturated at high initial concentration rate.[38] Although Pb(II) removal efficiency and biosorption capacity at equilibrium were not remarkably influenced by Fe(III), the rate at which Pb(II) biosorption took place was consistent.[39]

3.5. Biosorption isotherm

Equilibrium study for an adsorption system is frequently described using adsorption isotherms. It is generally defined as the ratio of the quantity adsorbed to that remaining in the solution at a fixed temperature and equilibrium conditions. Three isotherm equations tested to fit the experimental data as follows:

Langmuir equation: $\frac{C_e}{q_e}=\frac{1}{K_L.\theta}+\frac{C_e}{\theta}$ (3)

Freundlich equation: $\log q_e=\log K+\frac{1}{n}\log C_e$ (4)

Temkin equation: $q_e=\frac{RT}{b_T}\ln A_T+\left(\frac{RT}{b_T}\right)\ \ln C_e$ (5)

Where, q_e is the amount of heavy metal adsorbed at equilibrium (mg/g), and C_e is the equilibrium concentration of metal ions in the solution (mg/L). In each isotherm, constants or other parameters can be determined through the regression of the experimental data. For the Langmuir equation, θ (mg/g) is a measure of the adsorption capacity under the experimental conditions, and K_L is a constant related to the energy of adsorption. For the Freundlich equation, n indicates the bond energy between the metal ion and the adsorbent, and K is related to bond strength. For the Temkin equation, R is the universal gas constant (8.314 J/mol K), T is the temperature (K), b_T is the Temkin isotherm constant, and A_T is the Temkin isotherm equilibrium binding constant (L/g).

The linearized Langmuir, Freundlich, and Temkin isotherms for Pb(II) and Fe(III) removals using 1g/L of SMCM1 and SCM0.5 as biosorbents are shown in Figs 6, 7 and 8, respectively. The estimated model parameters with the correlation coefficient (R^2) for the different models are summarized in Table 2.

Fig 6(a) shows the Langmuir isotherm fitting for Pb(II) removal with different initial concentrations of 10, 20, 40, 60, 80, and 100 mg/L. As illustrated in Table 2, R^2 values of 0.9343 and 0.8825 are obtained for SCM0.5 and SMCM1, respectively. Data for Fe(III) adsorption at equilibrium time with the same concentration as that of Pb(II) are used to fit the linear plot of the Langmuir isotherm (Fig 6(b)). As shown in Table 2, the data for SMCM1 and SCM0.5 satisfactorily fit the Langmuir isotherm with $R^2 > 0.988$ for Fe(III). The R^2 values show that the results for Fe(III) show a more satisfactory fitting.

Fig 7 shows the Freundlich isotherms for Pb(II) and Fe(III) biosorption on OPF-based biosorbents (SMCM1 and SCM0.5) with various initial concentrations of 10, 20, 40, 60, 80, and 100 mg/L. Fig 7(a) shows the Freundlich isotherm fitting for Pb(II) removal. The data show satisfactory fitting to the Freundlich isotherm, with $R^2 > 0.985$ for both biosorbents. Fig 7(b) shows the Freundlich isotherm fitting for Fe(III) removal. The correlation coefficients (R^2) for the Freundlich isotherm are also listed in Table 2. R^2 values of 0.966 and 0.830 are obtained for SCM0.5 and SMCM1, respectively. These results show rather unsatisfactory fitting for Fe(III) while satisfactory fitting for Pb(II).

The linearized Temkin isotherms of Fe(III) and Pb(II) in the solution are presented in Figs 8(a) and 8(b), respectively. Fig 8(a) shows the Temkin isotherm fitting for Pb(II) removal. R^2 values of 0.878 and 0.840 are obtained for SCM0.5 and SMCM1, respectively, for Pb(II) removal. Based on Table 2, the data for Fe(III) adsorption significantly fit the Temkin isotherm with $R^2 > 0.839$ for all biomass types.

The applicability of the present data in the three isotherm models follow the order of Langmuir > Temkin > Feundlich for Fe(III) and Freundlich > Langmuir > Temkin for Pb(II). As suggested by data in Table 2, the adsorption mechanisms for removing Pb(II) and Fe(III) were different.

One of the essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless separation parameter R_L, as follows:

$$\mathrm{R_L} = \frac{1}{1 + \mathrm{K_L C_0}} \tag{6}$$

Where, K_L is the Langmuir constant. R_L values at different initial concentrations of 10, 20, 40, 60, 80, and 100 mg/L are presented in Table 3 for both metals. In both treatment methods, the

R_L values for Pb(II) and Fe(III) removals range from 0.076 to 0.575 and from 0.064 to 0.497, respectively. In this context, a lower R_L value reflects that adsorption is more favorable. The R_L value obtained indicates that the biosorption process is a favorable one ($0 < R_L < 1$). [40]

3.6. Kinetics study

To analyze the adsorption kinetics of heavy metal ions, pseudo-first-order and pseudo second-order reaction equations are applied to the experimental data. The first-order rate equation is one of the most widely used equations for the adsorption of a solute from an aqueous solution and is represented as follows:

$$\ln (q_\mathrm{e} - q_\mathrm{t}) = \ln q_\mathrm{e} - K_{1\mathrm{ad}}\mathrm{t} \tag{7}$$

where, q_e is the mass of metal ions adsorbed at equilibrium (mg/g), q_t is the mass of metal ions adsorbed at time t (mg/g), and K_{1ad} is the first-order reaction rate constant (L/min). The pseudo-first-order reaction considers the rate of occupation of the adsorption sites to be proportional to the number of unoccupied sites. A plot of $ln\ (q_e - q_t)$ versus t shows a straight line to confirm the applicability of the first-order rate equation (Fig 9). Meanwhile, the pseudo-second-order equation based on adsorption equilibrium capacity can be expressed as follows:

$$\frac{1}{\mathrm{q_t}} - \frac{1}{\mathrm{q_e}} = \frac{1}{\mathrm{K_{2ad}q_e^2t}} \tag{8}$$

Where, K_{2ad} is the second-order reaction rate equilibrium constant (g/mg min). A plot of $(1/q_e - 1/q_t)$ versus $1/t$ [41] should yield a linear relationship for the applicability of the second-order kinetic model (Fig 10).

The correlation coefficients of Pb(II) and Fe(III) for the pseudo-first-order kinetic model and pseudo-first-order were determined and compared with the R^2 obtained for the pseudo second-order kinetic model in Table 4. As shown in Table 4, the correlation coefficients of the pseudo-second-order model are greater than that of the pseudo-first-order model. These results showed that the mechanism of the adsorption process was mainly controlled by chemisorption. Chemisorption may be the rate-limiting step, which involves valence forces from the sharing or exchange of electrons between the sorbate and the sorbent. [41-45]

4. Conclusions

Results in this study indicated that the pretreatment of OPF biomass could significantly improve the efficiency of biosorption process. NaCl and Na_2SO_4 were effective reagents for pretreatment of OPF biomass and could remarkably increase the removal of Pb(II) and Fe(III) from aqueous solutions by generating ionic exchange interactions. The SCM0.5 biosorbent exhibited the highest adsorption efficiency among all the pretreated biomasses in this study. Under optimum conditions, SCM0.5 achieved 98% and 92% removal for Pb(II) and Fe(III), respectively. The biosorption process was a function of adsorbent dosage and agitation time. It is also observed that the total removal percentage of Pb(II) and Fe(III) decreased with increasing initial metal concentration although the exact amount of heavy metals adsorbed per unit mass of biosorbent increased with the increase in initial concentration. It was proven that the pretreated OPF was effective for the biosorption of Pb(II) and Fe(III) from aqueous solutions. The pretreatment process that used NaCl and Na_2SO_4 could significantly improve the biosorption efficiency of OPF. The biosorption process was also a function of biosorbent dosage and agitation time. The SCM0.5 biosorbent exhibited the highest biosorption efficiency among all the pretreated biomasses used. Under optimum conditions, 98% Pb(II) and 92% Fe(III) were removed from the aqueous solutions using the SCM0.5 biosorbent. The equilibrium adsorption data satisfactorily fit isotherms in the order of Langmuir > Temkin > Feundlich isotherms for Fe(III) and Freundlich > Langmuir > Temkin isotherms for Pb(II). Adsorption kinetics also follow the pseudo-second-order kinetic model which exhibits satisfactory fitting values of $R^2 > 0.880$ for all biomass types. The results of this study could be useful for designing environmental friendly wastewater treatment plants based on biosorption process.

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Tables:

Table 1. The chemically pretreatment scheme and the obtained biosorbents

Concentrations and modification means	Temperature (° C)	Processing Time (h)	Sample code
1.0 molar Na_2SO_4	25	24	SM1
1.0 molar NaCl	25	24	CM1
0.5 molar NaCl & 0.5 molar Na_2SO_4	25	24	SCM0.5
SM1 & CM1 1:1	25	-	SMCM1

Table 2. Estimated isotherm models for Pb(II) and Fe(III) and their constants for two types of adsorbents

Heavy metal	Adsorbent type	Langmuir equation $\frac{C_e}{q_e}=\frac{1}{b.\theta}+\frac{C_e}{\theta}$			Freundlich equation $\log q_e = \log K + \frac{1}{n} logC_e$			Temkin equation $q_e = a + b \ln C_e$		
		R^2	θ	b	R^2	K	$\frac{1}{n}$	R^2	a	b
Pb (II)	SCM0.5	0.9343	126.582	0.122	0.9854	13.391	1.412	0.8775	20.607	18.922
	SMCM1	0.8825	129.87	0.074	0.9948	9.669	1.391	0.8395	12.837	17.931
Fe (III)	SCM0.5	0.9887	107.527	0.145	0.9662	23.529	2.434	0.9838	7.8843	23.896
	SMCM1	0.9893	114.942	0.101	0.83	20.854	2.246	0.839	2.9885	25.136

Table 3. Different values of R_L for two adsorbent types at different concentrations of lead (II) and iron (III)

Heavy metal	Concentration	R_L values for different types of adsorbent	
		SCM0.5	SMCM1
Pb (II)	10	0.450	0.575
Fe (III)		0.408	0.497
Pb(II)	20	0.291	0.403
Fe (III)		0.256	0.331
Pb(II)	40	0.170	0.252
Fe (III)		0.147	0.198
Pb(II)	60	0.120	0.184
Fe (III)		0.103	0.142
Pb(II)	80	0.093	0.144
Fe (III)		0.079	0.110
Pb(II)	100	0.076	0.119
Fe (III)		0.064	0.090

Table 4. Estimated kinetic models and their constants for different types of biosorbent

	Types of adsorbent	1st order		2nd order	
		R^2	K_{1ad}	R^2	K_{2ad}
Pb (II)	SCM0.5	0.9532	0.0286	0.9955	0.0013
	SMCM1	0.8684	0.025	0.8805	0.0012
	SM1	0.9092	0.0138	0.9914	0.0009
	CM1	0.9621	0.0182	0.9729	0.0018
Fe (III)	SCM0.5	0.9707	0.024	0.9995	0.0035
	SMCM1	0.9697	0.0259	0.9745	0.0027
	SM1	0.9678	0.0206	0.9965	0.00005
	CM1	0.9155	0.0206	0.9904	0.0012

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Fig. 1. The SEM morphology of biosorbents a) SM1 before biosorption, b) SM1 after biosorption, c) CM1 before biosorption, d) CM1 after biosorption, e) SCM0.5 before biosorption, f) SCM0.5 after biosorption, g) SMCM1 before biosorption and h) SMCM1 after biosorption.

Fig. 2. The EDX micrographs of biosorbents a) SM1 before biosorption, b) SM1 after biosorption, c) CM1 before biosorption, d) CM1 after biosorption, e) SCM0.5 before biosorption, f) SCM0.5 after biosorption, g) SMCM1 before biosorption and h) SMCM1 after biosorption.

Fig. 3. Effect of amount of biosorbent on the biosorption of (a) Pb(II) and (b) Fe(III) in the solution. (pH=5-6, initial ions concentration=500 mg/L and contact time=40 min)

Fig. 4. Effect of contact time on the biosorption of (a) Pb(II) and (b) Fe(III) in the solution. (pH=5-6, initial ions concentration=500 mg/L, biosorbent dosage for SCM0.5 and SMCM1=1.25 g/L and for SM1 and CM1=1 g/L)

Fig. 5. Effect of initial metal concentration on the biosorption of (a) Pb(II) and (b) Fe(III) in the solution. (pH=5-6, biosorbent dosage=1 g/L and contact time=20 min)

Fig. 6. Langmuir isotherm plot for biosorption of Pb(II) and Fe(III) onto different types of biosorbent, (a) Pb(II), (b) Fe(III). (pH=5-6, biosorbent dosage=1 g/L and contact time=20 min)

Fig. 7. Freundlich isotherm plots for biosorption of Pb(II) and Fe(III) onto different types of biosorbent, (a) Pb(II), (b) Fe(III). (pH=5-6, biosorbent dosage=1 g/L and contact time=20 min)

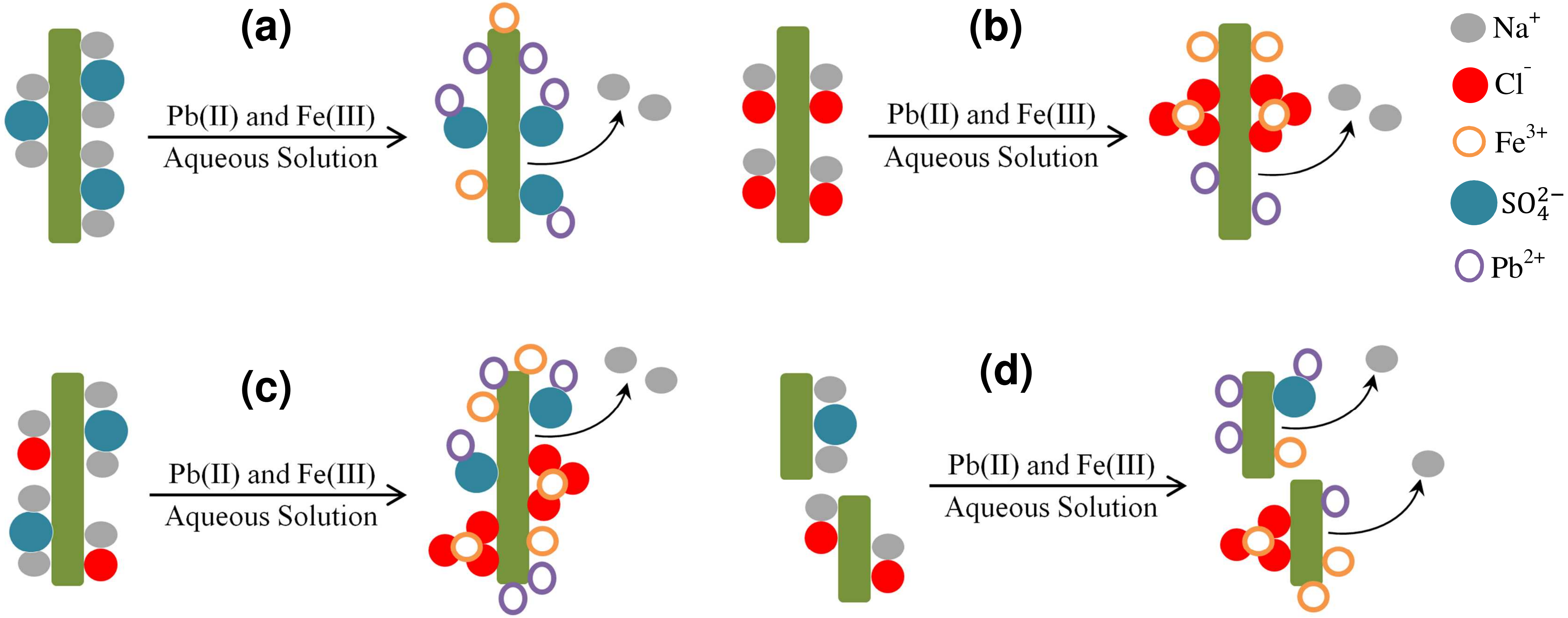
Fig. 8. Temkin isotherm plots for biosorption of Pb(II) and Fe(III) onto different types of biosorbent, (a) Pb(II) (b) Fe(III). (pH=5-6, biosorbent dosage=1 g/L and contact time=20 min)

Fig.9. Pseudo-first order plots for biosorption of Pb(II) and Fe(III) onto different types of biosorbent, (a) Pb(II), (b) Fe(III). (pH=5-6, biosorbent dosage=1 g/L and initial ions concentration=500 mg/L)

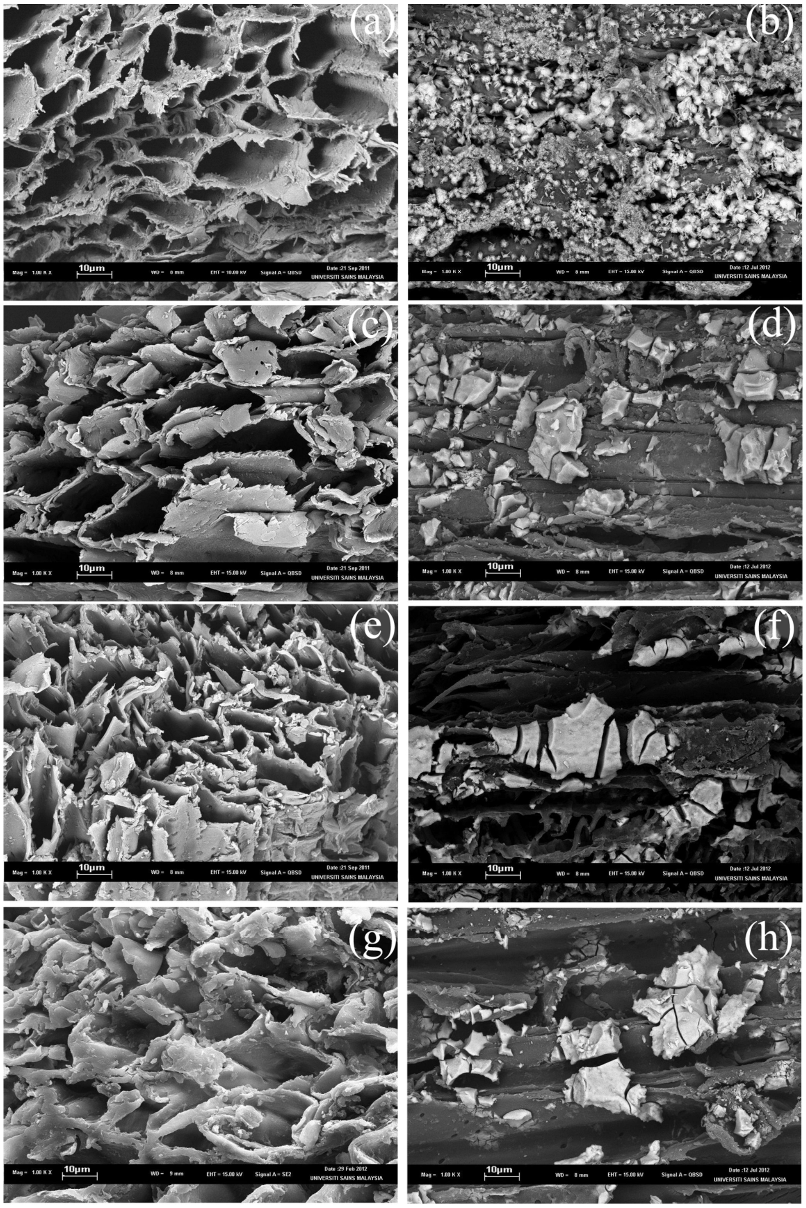
Fig. 10. Pseudo-second order plots for biosorption of Pb(II) and Fe(III) onto different types of biosorbent, (a) Pb(II), (b) Fe(III). (pH=5-6, biosorbent dosage=1 g/L and initial ions concentration=500 mg/L)

List of Scheme:

Scheme 1. Biosorption mechanism on a)SM1, b)CM1, c)SCM0.5 and d)SMCM1



Scheme 1. Biosorption mechanism on a) SM1, b) CM1, c) SCM0.5 and d) SMCM1



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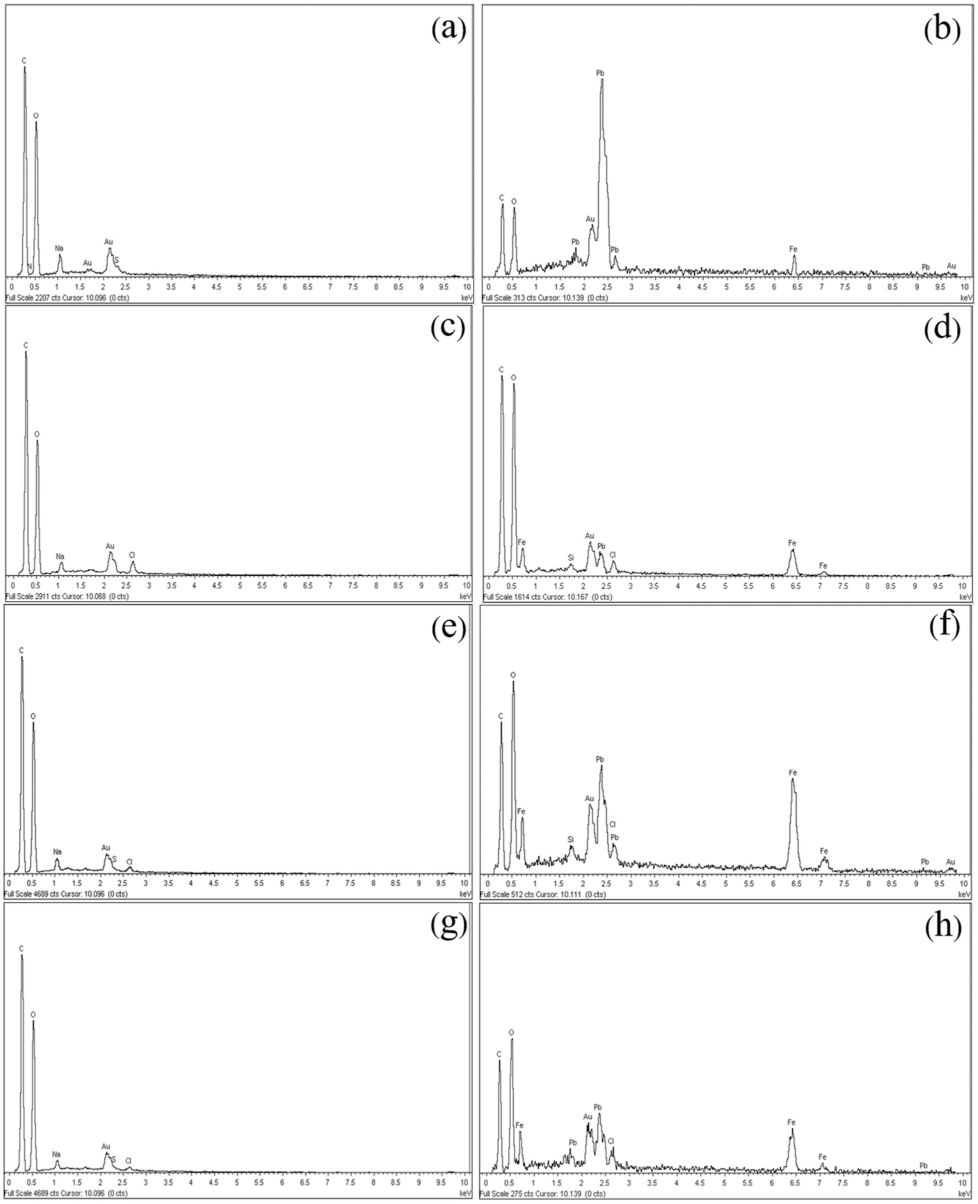

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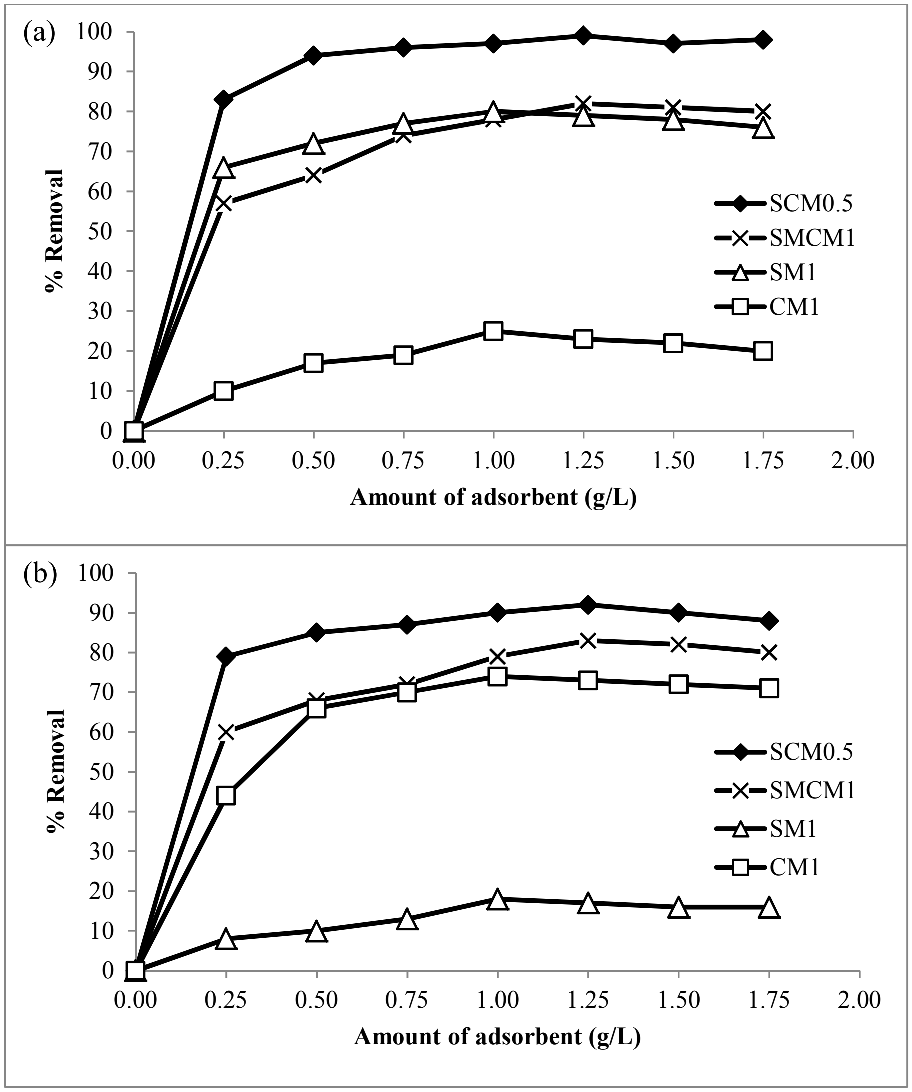

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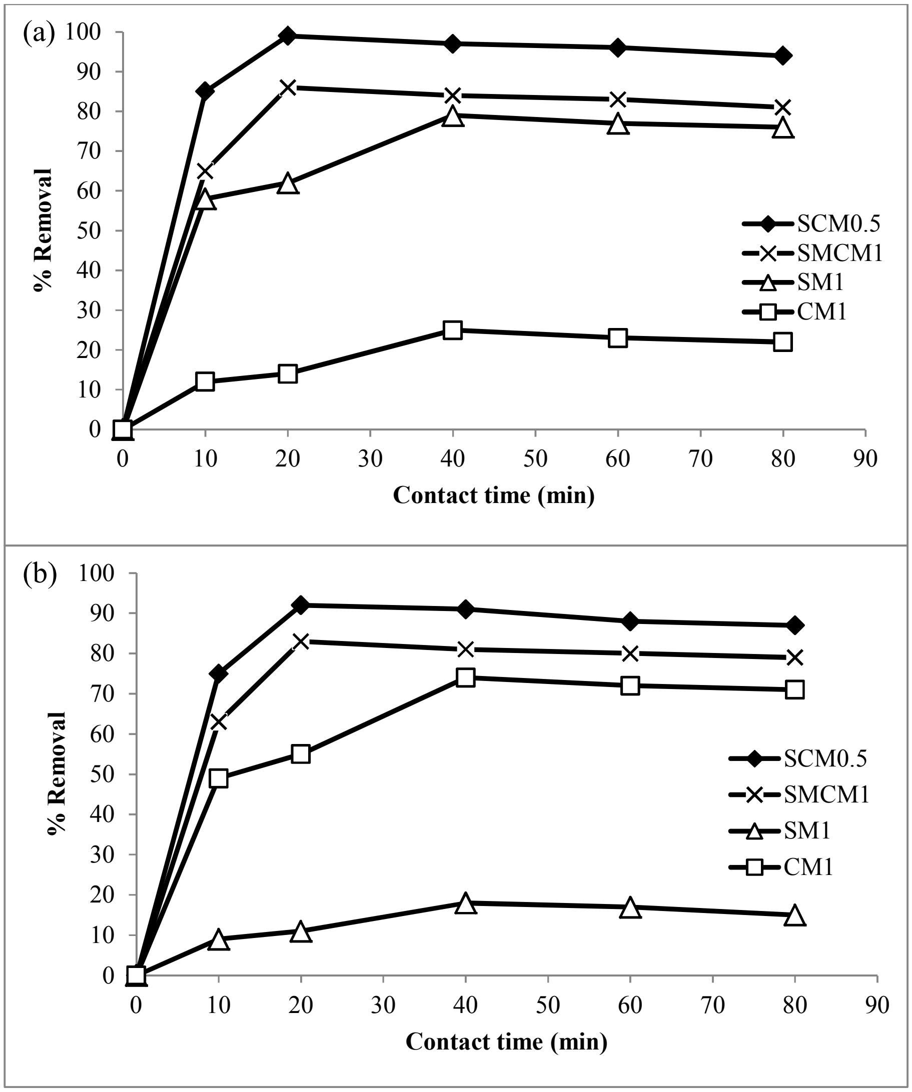

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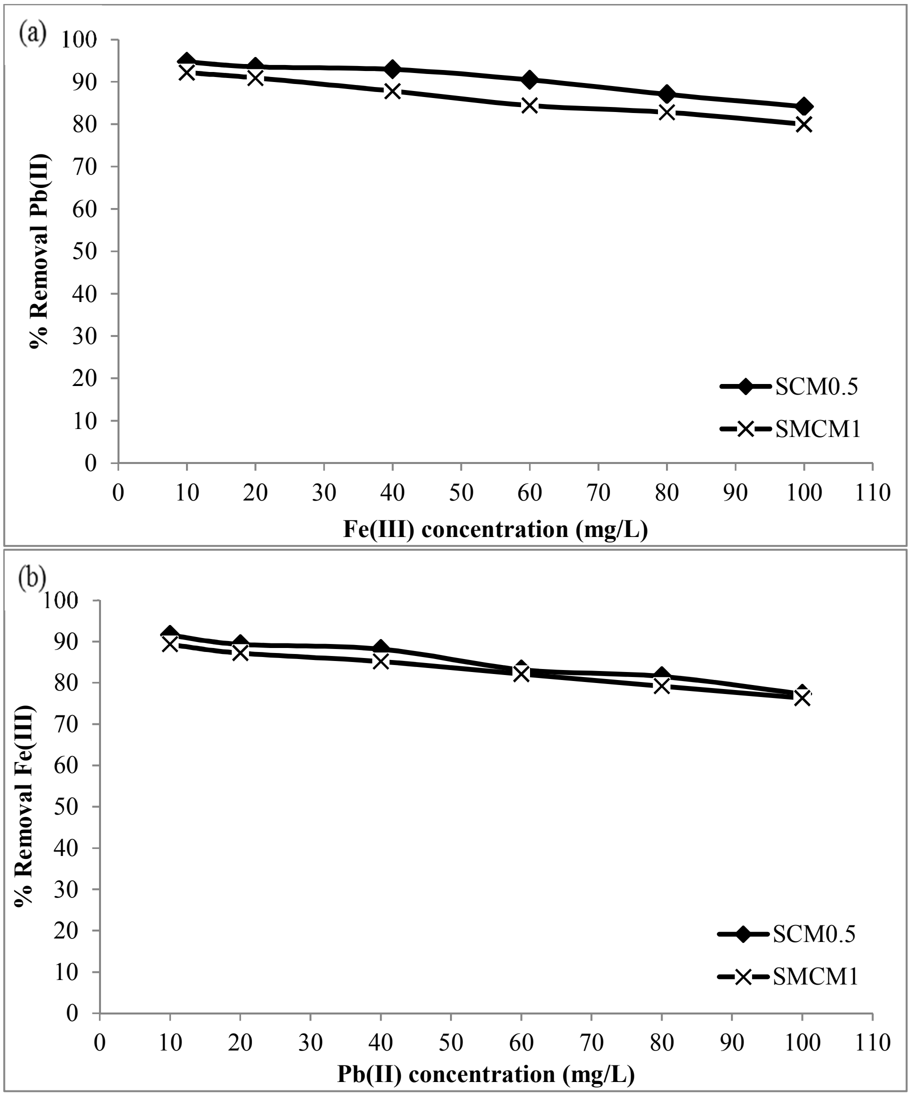

Fig. 5. Effect of initial metal concentration on the removal of (a) Pb(II) and (b) Fe(III) in the solution. (pH=5-6, biosorbent dosage=1 g/L and contact time=20 min)

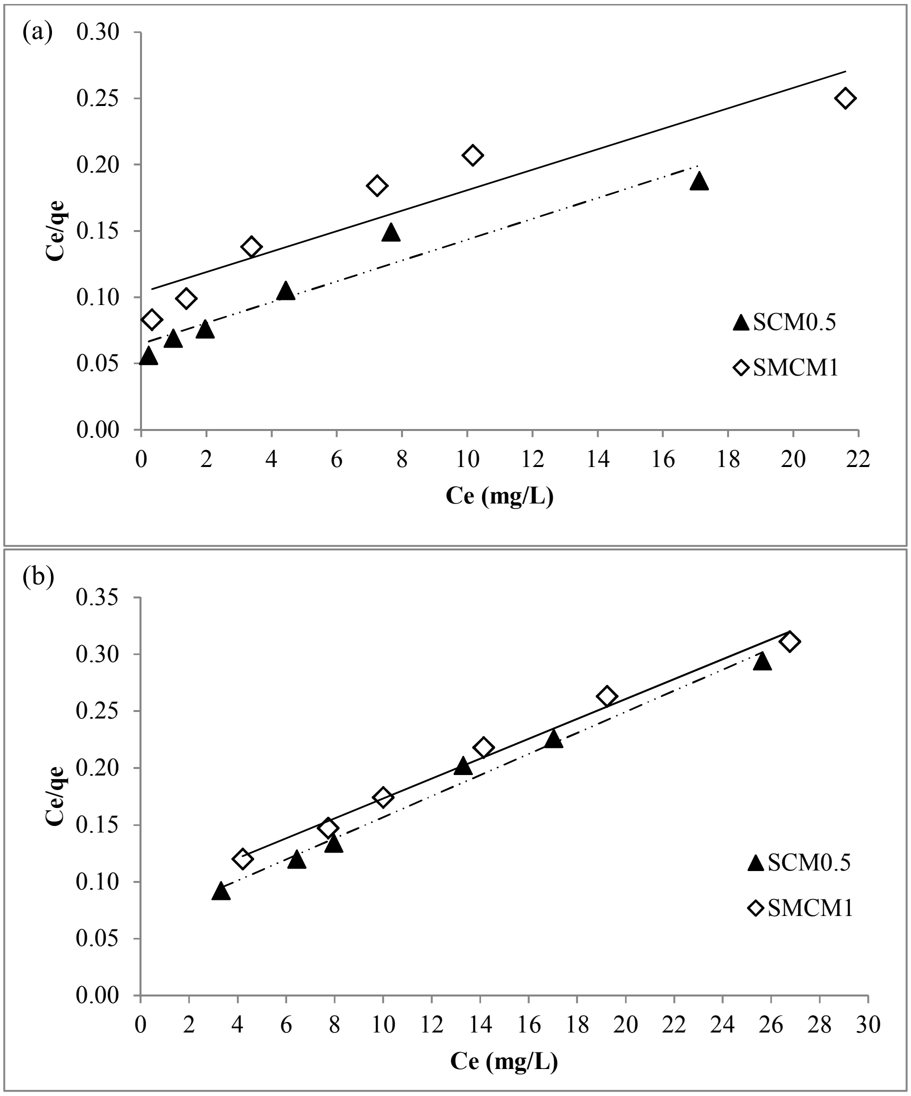

Fig. 6. Langmuir isotherm plot for biosorption of Pb(II) and Fe(III) onto different types of biosorbent, (a) Pb(II), (b) Fe(III). (pH=5-6, biosorbent dosage=1 g/L and contact time=20 min)

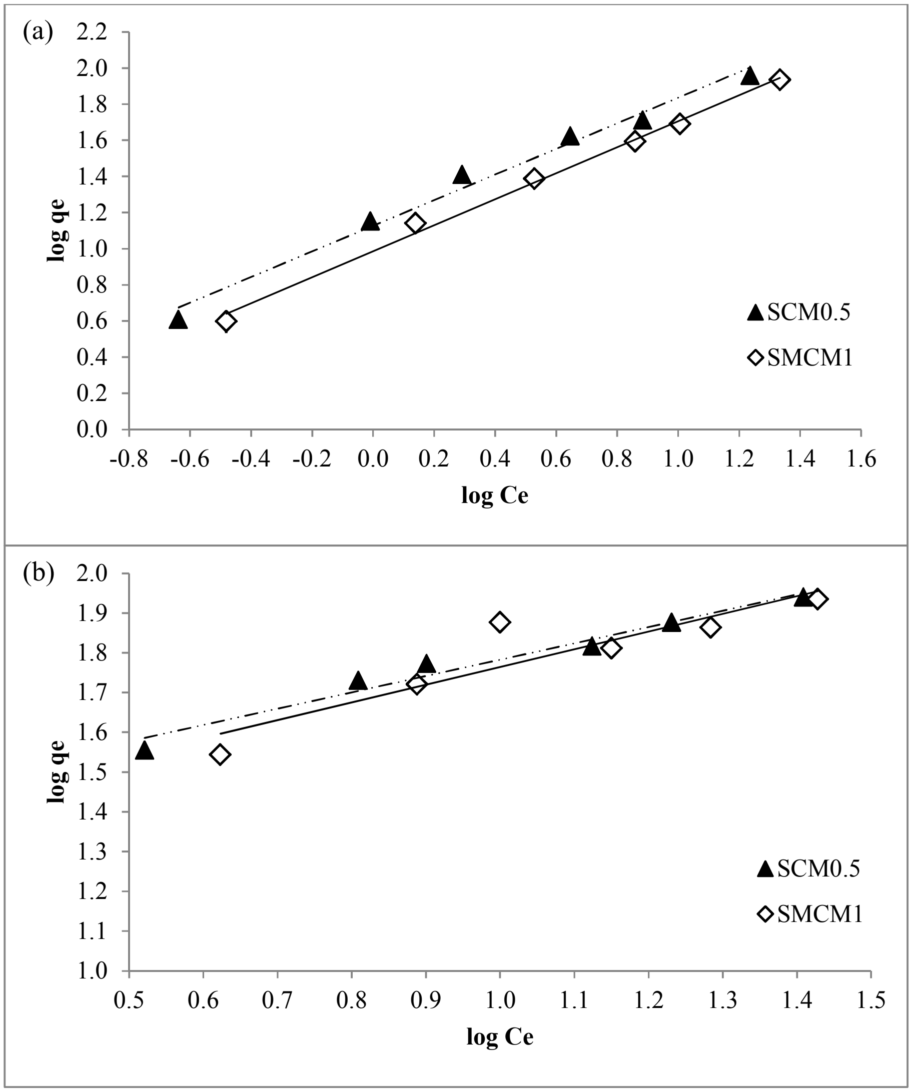

Fig. 7. Freundlich isotherm plot for biosorption of Pb(II) and Fe(III) onto different types of biosorbent, (a) Pb(II), (b) Fe(III). (pH=5-6, biosorbent dosage=1 g/L and contact time=20 min)

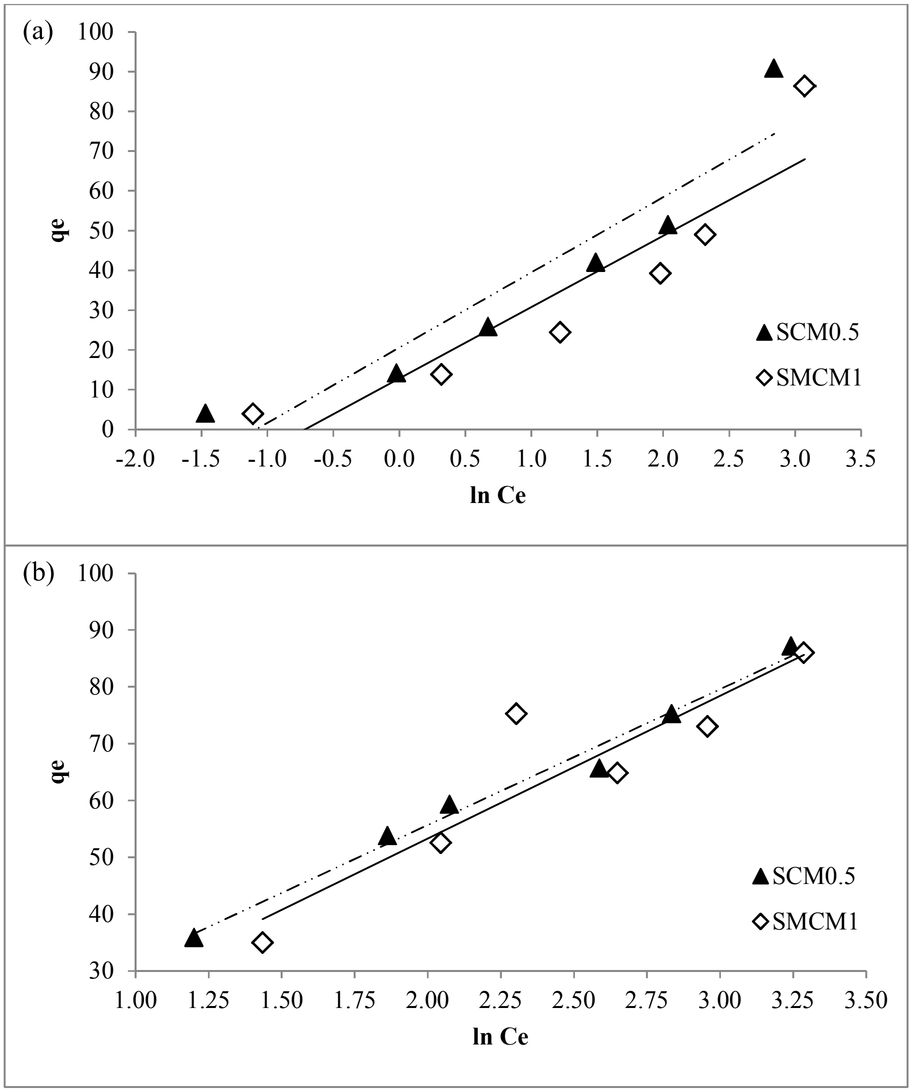

Fig. 8. Temkin isotherm plot for biosorption of Pb(II) and Fe(III) onto different types of biosorbent, (a) Pb(II) (b) Fe(III). (pH=5-6, biosorbent dosage=1 g/L and contact time=20 min)

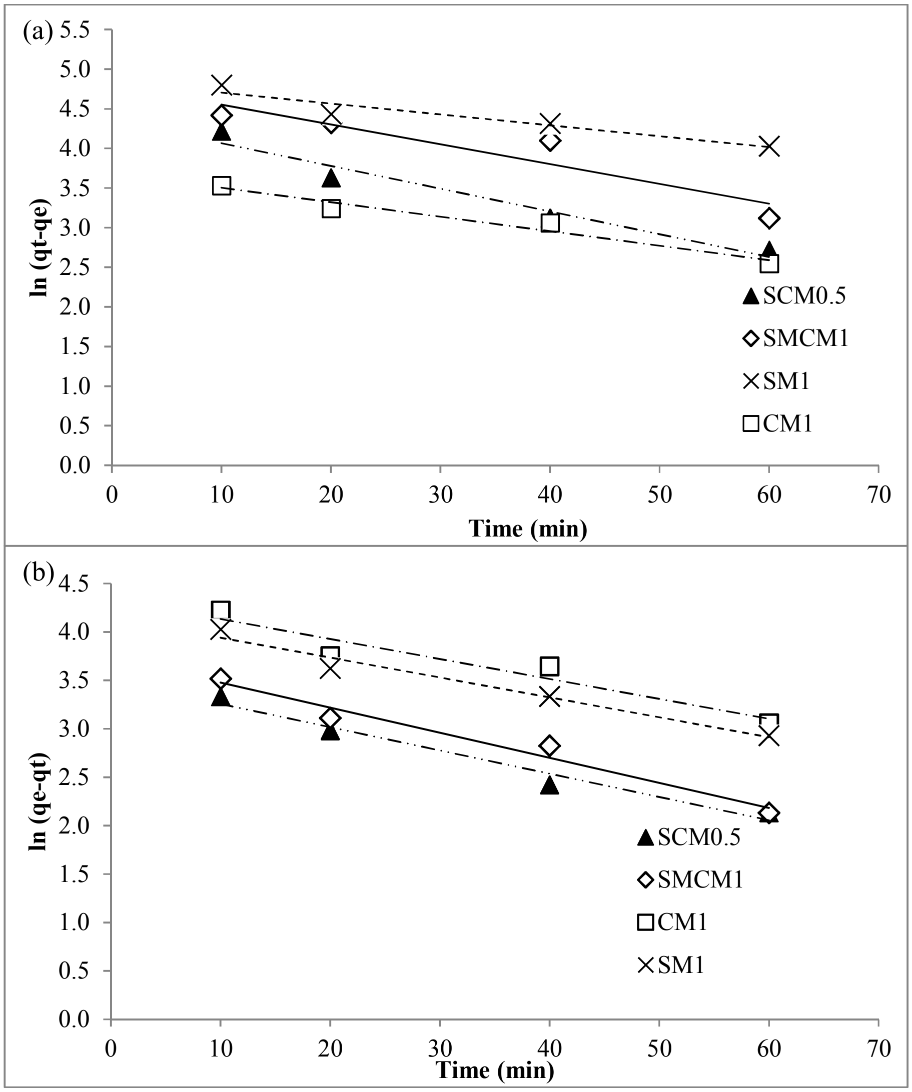

Fig. 9. Pseudo-first order plot for biosorption of Pb(II) and Fe(III) onto different types of biosorbent, (a) Pb(II), (b) Fe(III). (pH=5-6, biosorbent dosage=1 g/L and initial ions concentration=500 mg/L)

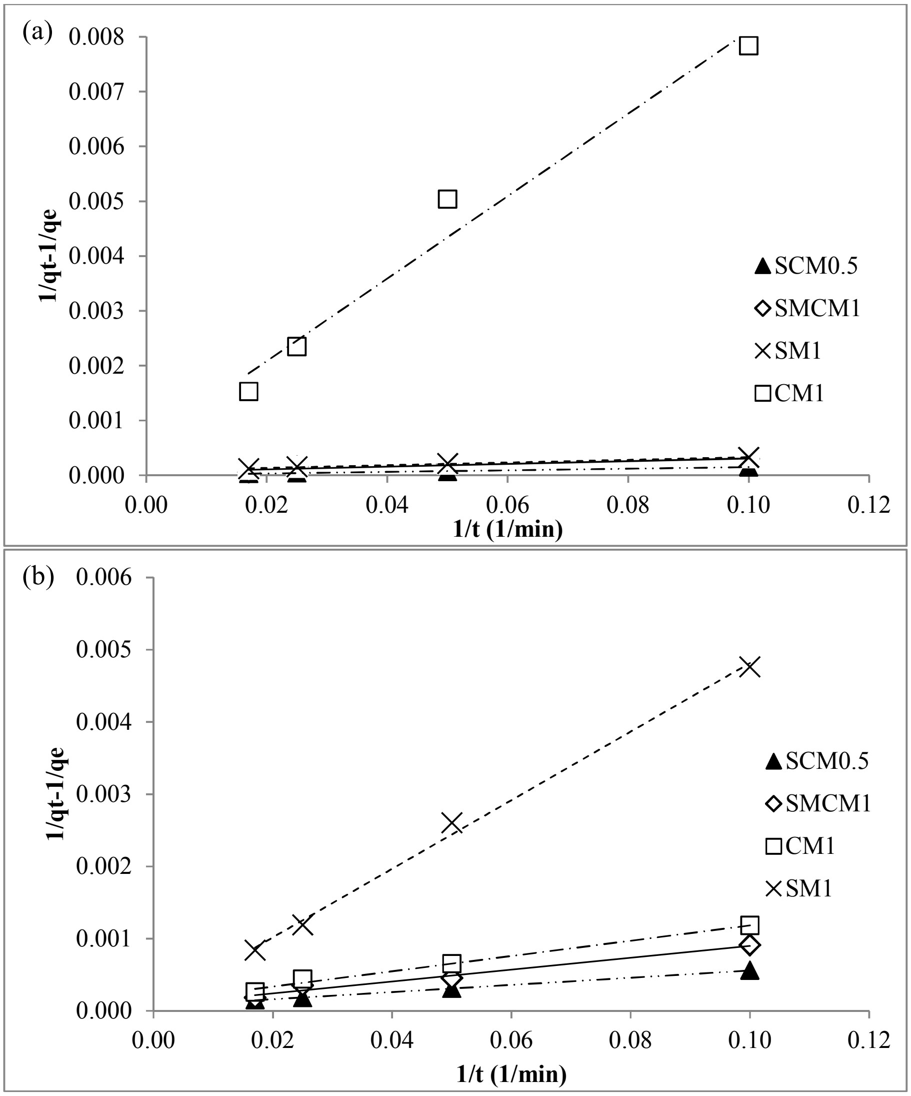

Fig. 10. Pseudo-second order plot for biosorption of Pb(II) and Fe(III) onto different types of biosorbent, (a) Pb(II), (b) Fe(III). (pH=5-6, biosorbent dosage=1 g/L and initial ions concentration=500 mg/L)