Exploring the lead (Pb) sorption potentials of biosorbents from wastewater

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ABSTRACT

Preservation and conservation of water and its quality from various sources of pollution is a task of greater concern nowadays. Heavy metal pollution chiefly lead (Pb) causes various environmental disequilibrium and health hazards. Utilisation of agricultural byproducts for the removal of Pb from such contaminated water has been studied widely in recent decades and the effect of sorbent dosage, initial Pb^{2+} concentrations, and incubation time intervals on Pb adsorption was described using isotherm models in this study. It was inferred from the results that, FYM had higher Pb adsorption capacity (7.00 mg g^{-1}) than coirpith (2.73 mg g^{-1}) which increased with increasing time intervals from 0 to 7.61 mg g^{-1} for FYM and 3.71 mg g^{-1} for coirpith. The adsorption capacity of FYM increased from 0.997 to 15.7 mg g^{-1} and 0.71 to 5.61 mg g^{-1} in coirpith when the initial Pb concentration increased from 100 to 2000 mg kg^{-1}. Both Langmuir and Freundlich adsorption isotherm explained the sorption process of both the sorbents. Hence, it could be concluded that, FYM is the effective sorbent which can be utilized for the removal of Pb from wastewater.

Keywords: Lead; FYM; Coirpith; adsorption capacity; isotherms.

1. INTRODUCTION

Shrinking water availability day by day due to population explosion and industrialisation has necessitated the prerequisite for preserving the existing water resources and their quality. On the other hand, increasing pollution of ground and surface water due to different anthropogenic activities has increased the risk of causing diseases to human beings and other creatures which get exposed to these contaminated waters. Among the pollutants, presence of heavy metal ions in the aquatic environment is a matter of greater importance because of their toxic, non-biodegradable nature whose levels of discharge keeps on increasing (Kumar, 2014). Heavy metals exist commonly in industrial wastewaters discharged from mining operation, tanneries, metal plating, petroleum refining, car radiator manufacturing, painting, batteries, printing, photographic, smelting, paper, pesticides, fertilizer, etc. (Ngah and Hanifah 2008; Zhang et al, 2014). These toxic metal ions (Cr, Ni, Co, Pb, Hg, As, Cd, Cu, Zn) persist in nature and accrues in living tissues (Ngah and Hanifah, 2008; Acharya et al, 2018). Lead (Pb) is one such toxic heavy metal ranking 2nd in the list of toxic substance given by ATSDR. Disposal of heavy metals like Pb directly or indirectly into soils and waters leads to significant environmental and human health risks. The Pb preferably accumulates in kidney, brain, muscles, and bones and causes hypertension, kidney and brain damage in human beings.

Removal of these pollutants from aquatic ecosystems has been a key area of research over the last few decades. The remediation strategy is developed based on the biological, chemical, physical and thermal properties of these pollutants and the methods in practice include ion exchange, biodegradation, oxidation, precipitation, coagulation, adsorption, filtration, flocculation, electrodialysis, irradiation, membrane process, reverse osmosis, distillation, ozonation, and solvent extraction (Syuhadah and Rohasliney 2012; Saroj et al, 2015; Tran et al, 2015; Acharya et al, 2018; Priya, 2018). Unfortunately, most of these techniques are costly, less flexible, has low efficiency and depicts the possibility of producing secondary pollutants (Syuhadah and Rohasliney, 2012). Among different remediation methods, adsorption could be considered as an effective technique which is comparatively inexpensive, simple, rapid, easy to perform and the ease of their availability (Chen et al, 2012; Sadon et al, 2012). The commonly used synthetic sorbents are of high cost and short life. Natural mineral sorbents have low adsorption capacity and their availability is limited which might end up in over-exploitation of these minerals leading to new environmental issues (Li et al, 2016). Agricultural byproducts with appropriate modification could be employed as an effective adsorbent for the removal of heavy metals ions from wastewater (Pellera et al, 2012). These organic materials possess various active binding sites, such as carboxyl, hydroxyl, amine, phenolate and thiol groups, which complexes or exchange metals, thus serving as potential sources to be used as sorbents (Tareq et al, 2019). In order to develop better sorption systems with these new and novel sorbents, establishment of most appropriate equilibrium correlation *viz*., adsorption isotherm becomes indispensable since it aids in the computation of adsorption parameters and allows the comparison of adsorbent behaviours in the developed sorption systems (Srivastava et al, 2006; Gimbert et al, 2008).

Among the agricultural byproducts, Farm yard manure (FYM) is a high volume, low-cost disposal material which is used as plant nutrient source and also as a soil conditioner thus improving the soil quality. They possess a wide range of polymeric materials like cellulose, hemicellulose, lignin, protein and also semi decomposed and decomposed humic materials which possess many polar functional groups, making it a promising adsorbent for divalent metal cations (Kandah et al, 2003). Cocopeat has recently been utilized for the preparation of soilless media mixtures in protected cultivation of crops (Rout and Arulmozhiselvan 2019; Behera et al, 2022) as well as light weight substrate in green roofs, biofilters and vertical walls to support plant growth. It is also widely used as an oil absorbent for slippery floor (Premkumar and Vijayaraghavan, 2014; Vijayaraghavan et al, 2015). However, studies on the exploration of agricultural waste materials for heavy metal removal is meagre. Hence, this study has been formulated to know and compare the adsorption potentials of FYM and cocopeat incubated at different doses for the removal of Pb from contaminated water and to know the mechanisms undermining the sorption potentials of these materials.

2. MATERIALS AND METHODS

***2.1.* Pb standards and sorbents:** The Pb standards were prepared using analytical grade lead nitrate ($Pb(NO_3)_2$) salt and a stock solution of 2000 mg l^{-1} was prepared. Using the stock, different concentrations *viz*., 100, 250, 500, 1000 and 1500 mg l^{-1} of Pb^{2+} were prepared. The biosorbents *viz*., FYM was collected from Tamil Nadu Agricultural University farm, Coimbatore, shade dried, processed and used in the study. The coirpith was purchased from M/s. Siva enterprises, Namakkal, Tamil Nadu and both the sorbents were characterized for their basic physiochemical properties and Pb content.

***2.2.* Batch sorption experiments:** Batch sorption experiments were taken up at room temperature using various sorbents applied at three different doses (1, 2.5 and 5 g) in solutions having different initial Pb^{2+} concentrations (100, 250, 500, 1000, 1500 and 2000 mg l^{-1}) at successive time intervals (24, 48, 72, 96 and 120 hrs) to study their sorption and desorption potentials. The experiment was conducted in duplicates with a blank simultaneously to quantify the amount of Pb adsorbed and desorbed from solution by the sorbents.

***2.2.1.* Lead adsorption studies:** Batch sorption experiments were conducted at room temperature (25ºC) with various biosorbents for their adsorption potential at different sorbent dosage, contact time and Pb concentration. The sorption studies were conducted in 50 ml centrifuge tubes with specified doses of FYM (1, 2.5 or 5 g) in 25 ml and specified doses of coirpith (1, 2.5 or 5 g) in 50 ml solution known containing Pb concentration. The centrifuge tubes with biosorbents and Pb solution at different concentration was agitated on a mechanical shaker at 160 rpm for an appropriate contact time of 24, 48, 72, 96 and 120 hours, and centrifuged for 3 min at 5000 rpm. The supernatant was filtered using Whatman No.42 filter paper and analysed for residual metal ion concentration in an atomic absorption spectrophotometer (Model: GBC AvantaPM) with air-acetylene flame. Sufficient care was taken to prevent the loss of biosorbents while separating the supernatant, to conduct further studies. The experiment was conducted in duplicates with a blank simultaneously to quantify the Pb adsorbed by various biosorbents from solution. The quantity of Pb^{2+} adsorbed (q_e, mg g^{-1}) was estimated (Ray et al, 2020) using the following equation (1)

$$q_t = V \text{ x } \frac{C_0 - C_f}{m} \text{---------} (1)$$

where 'C_0' and 'C_f' are the concentrations of Pb^{2+} (mg l^{-1}) in initial and final solutions, respectively, 'V' is the volume of Pb^{2+} solutions added (25 ml) and 'm' is mass of the sorbent (g).

***2.2.2.* Adsorption isotherms:** An adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH (Foo and Hameed 2010). To comprehend the circulation of metal particles in the fluid and solid stages, distinctive isotherm models must be fitted with experimental equilibrium data. It describes how the adsorbate interacts with the adsorbent and offers an explanation on the nature and mechanism of the adsorption process (Limousin et al, 2007). The adsorption reaction reaches an equilibrium state and the isotherm indicates the distribution of adsorbate molecules between solid and liquid phase. Therefore, establishing most appropriate correlation of equilibrium curves is essential to optimize the conditions for proposing adsorption systems (Dharsana and Jose 2023). Hence, the data obtained from batch experiments were fitted to Langmuir and Freundlich isotherms models to identify the best fitted model so as to explain the retention and release characteristics of Pb in wastewater by FYM and coirpith.

***2.2.2.1.* Langmuir isotherm:** The Langmuir adsorption isotherm describes that, in the adsorbate-adsorbent system equilibrium, all adsorbed species interact only with one site and not with each other and adsorption is confined to a monolayer, where the surface of adsorbent is homogeneous and all sites on the surface have equal affinity for the adsorbate. The adsorption isotherm model outlined by Langmuir is furnished in the equation given below:

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \text{---------} (2)$$

Where, ‘q_m’ is the maximum monolayer coverage capacity (mg g^{-1}), ‘q_e’ is the amount of Pb adsorbed per gram of adsorbent at equilibrium (mg g^{-1}), ‘C_e’ is the concentration of Pb at equilibrium (mg L^{-1}) and ‘K_L’ is the constant representing the affinity of active binding sites (L mg^{-1}). The values of ‘q_m’ and ‘K_L’ were obtained from slope and intercept of plot between ‘C_e/q_e’ vs. ‘C_e’ (Langmuir 1918).

2.2.2.2. **Freundlich isotherm:** The adsorption isotherm proposed by Freundlich is commonly used for describing adsorption on heterogeneous surface (Dada et al, 2012) which is represented in the equation (3) below:

$$q_e = K_F C_e^{1/\eta} \text{---------} (3)$$

Where ‘K_F’ is the constant associated to adsorption capacity (mg g^{-1}) and ‘n’ is the intensity of adsorbent. The values of ‘n’ and ‘K_F’ were obtained from slope and intercept of Freundlich plot of log q_e vs. log C_e. The favourability of adsorption is indicated by the magnitude of exponent ‘η’.

2.3. **Statistical analysis:** The linear forms of six kinetic equations were fitted to the experimental data and the R^2 values and isotherm parameters were consequently attained from the fitted equations. The constants and parameters of all the isotherms were calculated using OriginPro 2022. The data is subjected to statistical analysis using SPSS software and simple variance analysis was done (ANOVA) using factorial completely randomized block design with three factorial arrangement (Pb^{2+} concentration, sorbent dose and incubation time interval) and two replications. The least significance test was used to detect the variations between means at $p < 0.005$.

3. RESULTS AND DISCUSSION

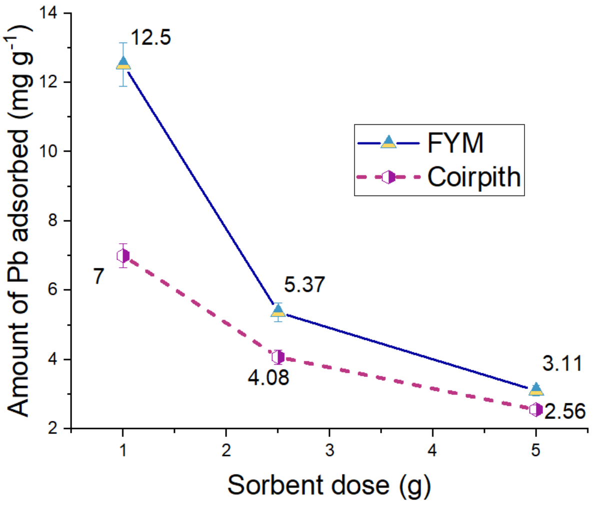
3.1. Lead (Pb^{2+}) adsorption as influenced by various factors

3.1.1. Sorbent dose: The effect of different sorbent dosage (1.0 - 5.0 g 25 mL^{-1}) on the adsorption capacity of lead at various contact time intervals was studied and the results were depicted in figure 1 a. The amount of Pb^{2+} adsorbed was decreased with increasing sorbent dosage in both the sorbent. The amount of Pb^{2+} adsorbed decreased from 12.5 to 3.11 mg g^{-1} in FYM and 7.0 to 2.56 mg g^{-1} in coirpith when the sorbent dose increased from 1 to 5 g. The adsorption capacity decreased with the increase in adsorbent dosage for both the adsorbents (figure 1a). As the sorbent dosage increased, the ratio of number of adsorption sites to the number of heavy metal ions also increases and there would be plenty of unabsorbed adsorption sites available (Kumar et al, 2011; Yarkandi 2014). It might also be the result from the aggregation of sorbents particles at higher dosages, thereby resulting in declined adsorbent surface area and an increase in diffusion path length (Chathuranga et al, 2014; Rezaei et al, 2022 and Ayodele et al, 2016).

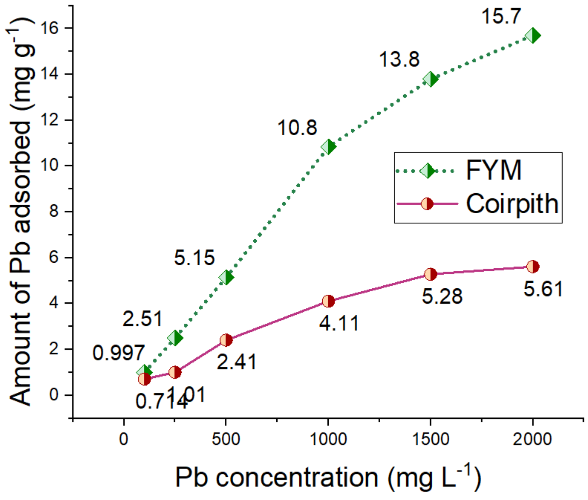
3.1.2. Initial Pb concentrations : The effect of initial Pb^{2+} concentrations in the solution on Pb adsorption capacity was studied and shown in figure1b. The quantity of Pb^{2+} adsorbed increased with increasing initial Pb concentrations and it was significantly higher in FYM than coirpith regardless of Pb concentrations. The amount of adsorbed Pb^{2+} varied from 0.997 to 15.7 mg g^{-1} in FYM and 0.714 to 5.61 mg g^{-1} in coirpith. The increase in Pb concentration resulted in increased number of available Pb ions per binding site in the adsorbent thus bringing a higher probability of Pb ion binding to the adsorbent. The probability of chemical interaction between the adsorbent and the adsorbate was enhanced by higher availability of Pb molecules in solution (Ahmad et al, 2012). Increasing initial Pb concentration, increases the interaction between the metal ions and sorbents, thus enhancing the availability of binding sites on the surface of sorbents (Bulut et al, 2018). These results corroborate with the findings reported by Yarkandi (2014) and Rezaei et al, (2022).

3.1.3. Time : The Pb^{2+} adsorption capacity was studied at different incubation time intervals for both the sorbents (Figure 1 c) and an increase in adsorption capacity was observed with the advancement of time. The adsorption capacity was noted to increase from 0 to 6.22 mg g^{-1} in FYM and 1.73 mg g^{-1} in coirpith within 24 hours of incubation. The initial faster adsorption was due to a rapid diffusion of ions from solution to external adsorbent surface, and the slower adsorption capacity in the second stage was possibly the result of diffusion of Pb ions into the adsorbent material (Harja et al, 2017). Upon saturation of adsorption sites, equilibrium is attained and adsorption capacity tends to increase at lesser rates (Shah et al, 2018). Similar observations were noted in this study where there is a slow and steady increase in adsorption rates (6.22 to 7.62 and 1.73 to 3.72 mg g^{-1} for FYM and coirpith respectively) from 24 to 120 hrs. These results are in line with the findings of Keleş et al, (2010), Sdiri et al, (2012), Harja et al, (2017) and Shah et al, (2018).

(a)



(b)



(c)

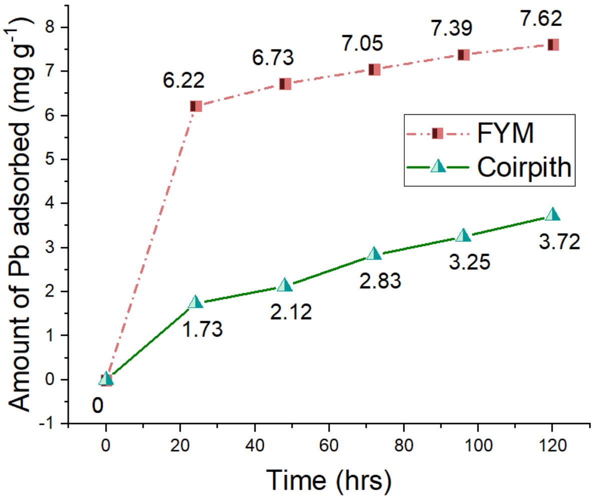


Figure 1. Adsorption rate of FYM and Coirpith as influenced by (a.) Sorbent doses (b.) Initial Pb concentrations and (c.) Time. Bars represent standard error; data are average of two replications; comparison of mean was done at 5% level.

3.2. Adsorption isotherms : The data gained from the experiment was fitted to Langmuir and Freundlich isotherm models to identify the best model to explain the Pb adsorption characteristics of sorbents (Table 1).

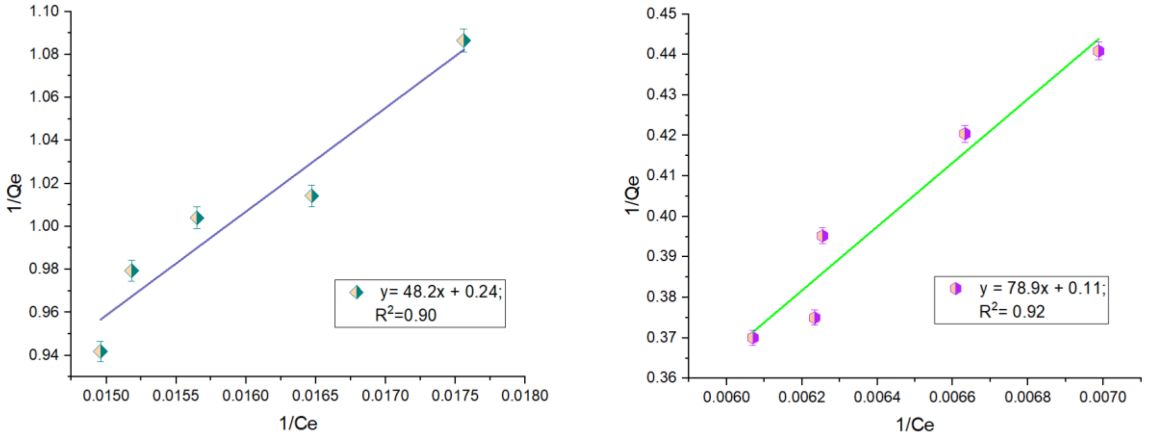
Table 1. Description of Pb sorption by FYM and Coirpith using Freundlich and Langmuir isotherms

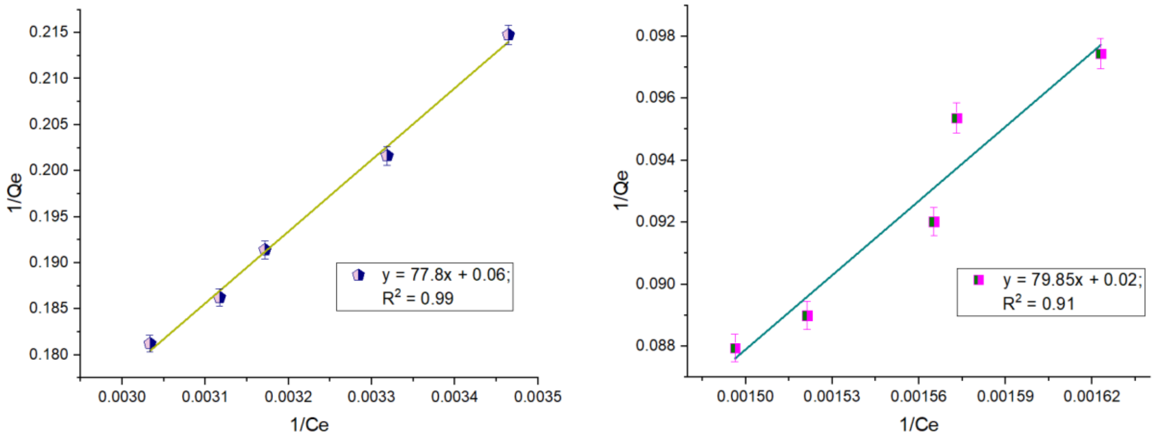
Sorbents	Pb conc (mg g^{-1})	Freundlich constants			Langmuir constants		
		K_F x 10^{-2}	η	R^2	Q_m	K_l x 10^{-3}	R^2
FYM	100	4.13	1.30	0.90**	4.25	4.88	0.90**
	250	0.41	0.79	0.92**	9.3	1.36	0.93**
	500	0.33	0.78	1.00**	18.0	0.72	0.99**
	1000	0.18	0.74	0.91**	31.4	0.40	0.91**
	1500	0.24	0.78	0.95**	48.3	0.26	0.95**
	2000	0.22	0.77	0.93**	48.0	0.26	0.92**
Coirpith	100	2.81	1.12	0.86**	14.1	1.11	0.85**
	250	2.05	1.09	0.96**	38.8	0.34	0.96**
	500	1.18	0.97	0.98**	2.53	2.83	0.97**
	1000	0.02	0.56	0.99**	9.03	1.07	0.98**
	1500	0.20	0.74	0.96**	7.54	1.05	0.95**
	2000	0.03	0.60	0.99**	58.4	0.28	0.99**

The coefficient of determination varied from 0.91** to 0.99** for FYM and 0.85** to

0.99** for coirpith indicating that, Langmuir isotherm explains the adsorption process well and denotes that adsorption takes place in a homogeneous monolayer (Kamal et al, 2021, Figure 2, 3). Testing with Langmuir isotherm where 'q_m' is the maximum monolayer coverage capacity and 'K_L' is the constant representing the affinity of active binding sites revealed a maximum monolayer coverage capacity ('q_m') of 4.25 to 48.3 and 2.53 to 58.4 mg g^{-1} in FYM and coirpith respectively. The monolayer coverage capacity was observed to increase with increasing initial Pb concentrations. However, the 'K_L' constant varied from 4.88 to 0.26 x 10^{-3} L mg^{-1} for FYM and 2.83 to 0.28 x 10^{-3} for coirpith and higher binding affinity was observed at lesser initial Pb concentrations and declined with increasing initial Pb concentrations. This confirms that, affinity of Pb towards both the sorbents decreased with increasing initial Pb concentrations (Mouflih et al, 2005 and Mouflih et al, 2006) which is agreeable with the findings of Nwachukwu and Pulford (2008) and Lekshmi and Divanshu (2014).

For Freundlich isotherm, the coefficient of determination, (R^2) varied from 0.91** to 1.00** for FYM and 0.86** to 0.99** for coirpith displaying that this model could also explain the adsorption process which takes place on a heterogeneous surface (Figure 4, 5). The Freundlich isotherm assumes that, adsorption occurs in multilayers and the amount of adsorbed material increases with increasing concentration of adsorbed material in solution (Weber 1972; Kumar 2014). Here, 'K_F' is the adsorption capacity constant (mg g^{-1}) and 'η' is the intensity of adsorbent. From the estimated results, the intensity of adsorbent ('η') varied from 0.74 to 1.30 for FYM and 0.56 to 1.12 for coirpith. Adsorption capacity constant 'K_F' varied between 4.13 to 0.18 x 10^{-2} mg g^{-1} and 2.81 to 0.03 x 10^{-2} mg g^{-1} in FYM and coirpith respectively. High K_F and η values indicate higher affinity of sorbent to sorption and desired levels of sorption process. Since both the isotherm models fit well, it can be concluded that, both ion exchange mechanism corresponding to Langmuir isotherm corresponds and adsorption-complexation reactions corresponding to Freundlich isotherm takes place in the system (Bulut 2007). These results are in line with the findings of Iftikhar et al, (2009), Huang et al, (2009), Borna et al, (2016).


(a) Pb concentration: 100 mg L^{-1} (b) Pb concentration: 250 mg L^{-1}


(c) Pb concentration: 500 mg L^{-1} (d) Pb concentration: 1000 mg L^{-1}

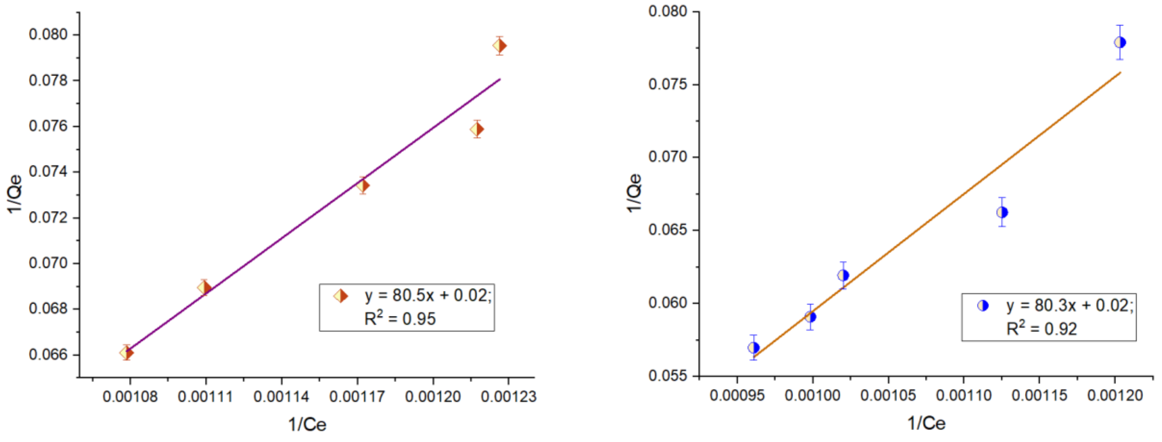
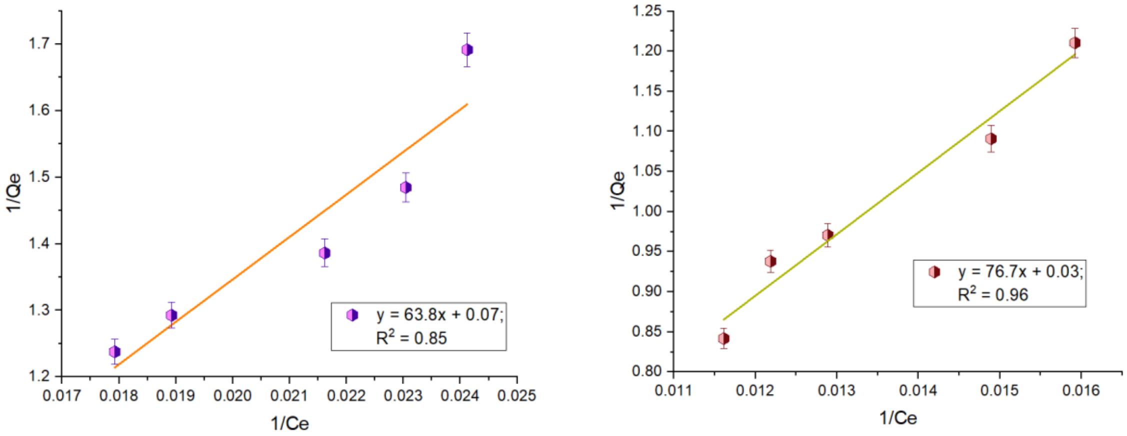

(e) Pb concentration: 1500 mg L^{-1} (f) Pb concentration: 2000 mg L^{-1}

Figure 2. Langmuir Adsorption Isotherm for describing the effect of FYM in removing Pb as influenced by varying initial Pb concentrations. Bars represent standard error; data are average of two replications; comparison of mean was done at 5% level

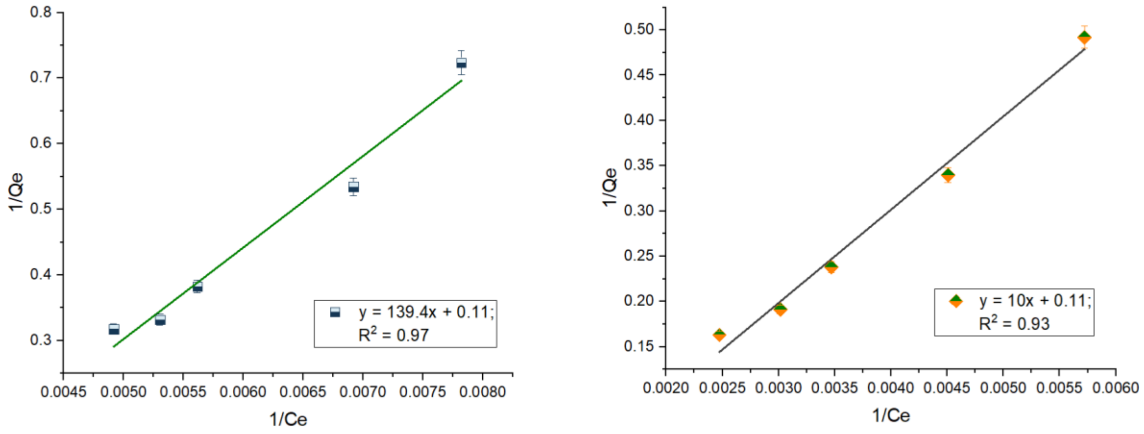
(a) Pb concentration: 100 mg L^{-1}

(b) Pb concentration: 250 mg L^{-1}



(c) Pb concentration: 500 mg L^{-1}

(d) Pb concentration: 1000 mg L^{-1}



(e) Pb concentration: 1500 mg L^{-1}

(f) Pb concentration: 2000 mg L^{-1}

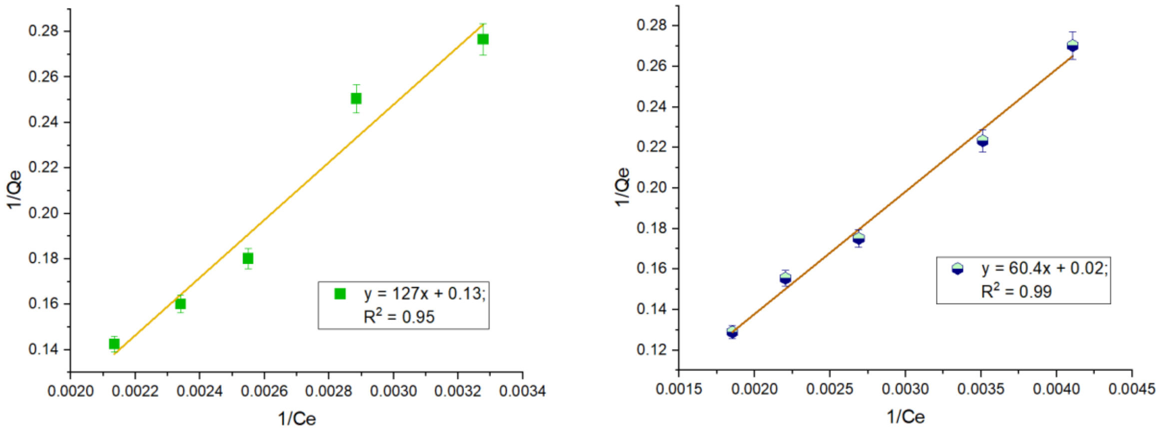
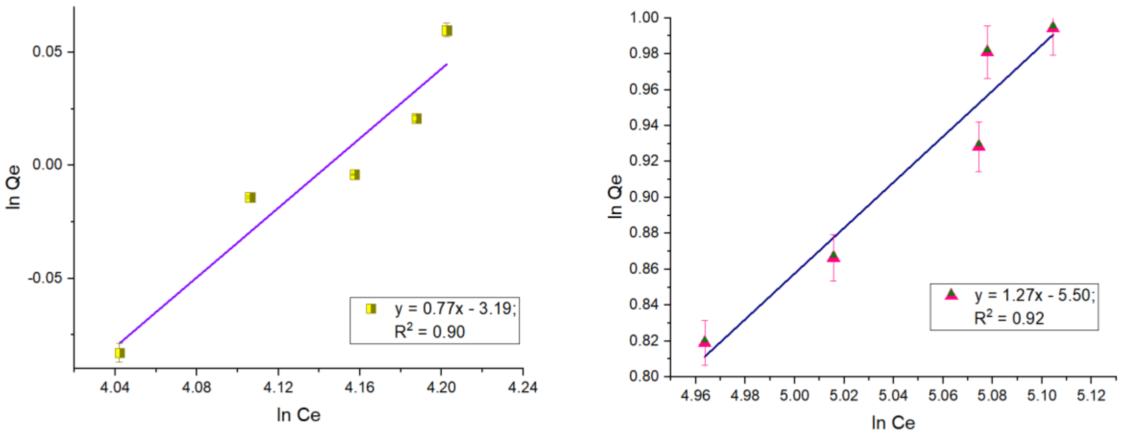
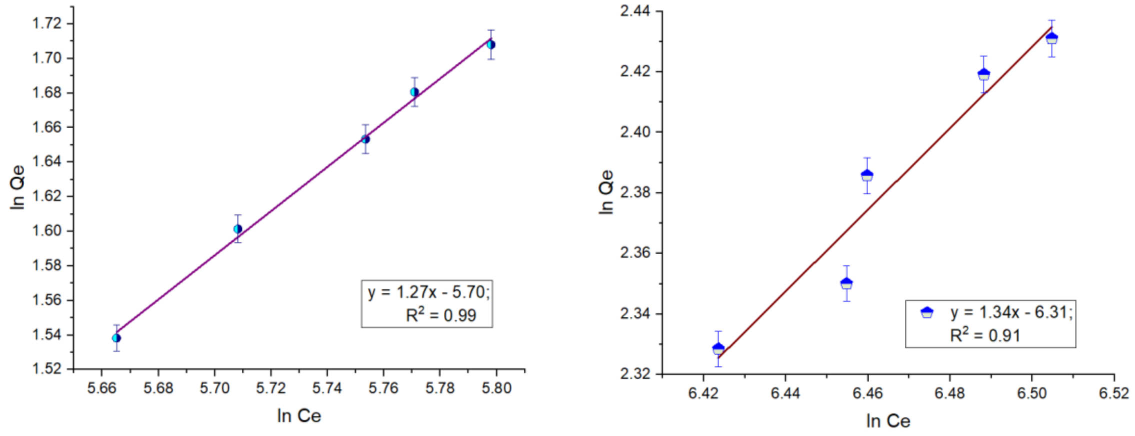


Figure 3. Langmuir Adsorption Isotherm for describing the effect of coirpith in removing Pb as influenced by varying initial Pb concentrations. Bars represent standard error; data are average of two replications; comparison of mean was done at 5% level



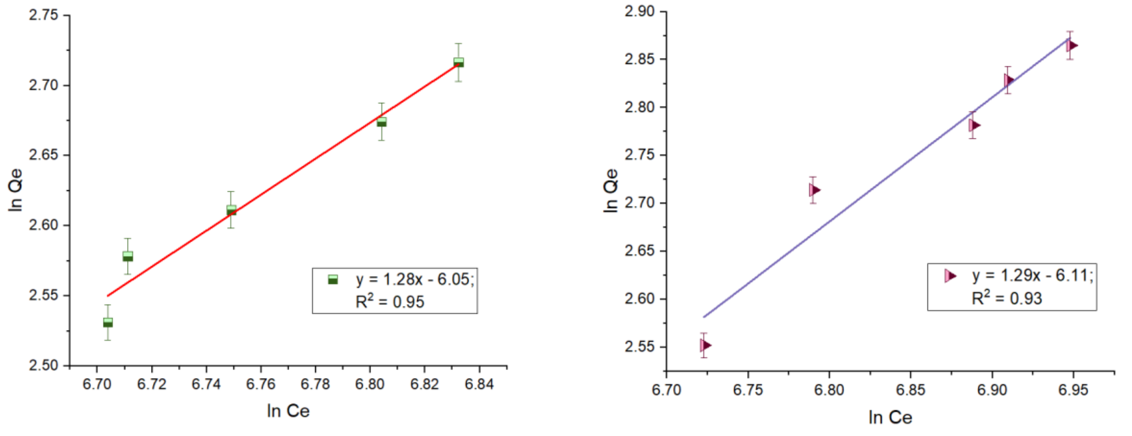
(a) Pb concentration: 100 mg L^{-1}

(b) Pb concentration: 250 mg L^{-1}



(c) Pb concentration: 500 mg L^{-1}

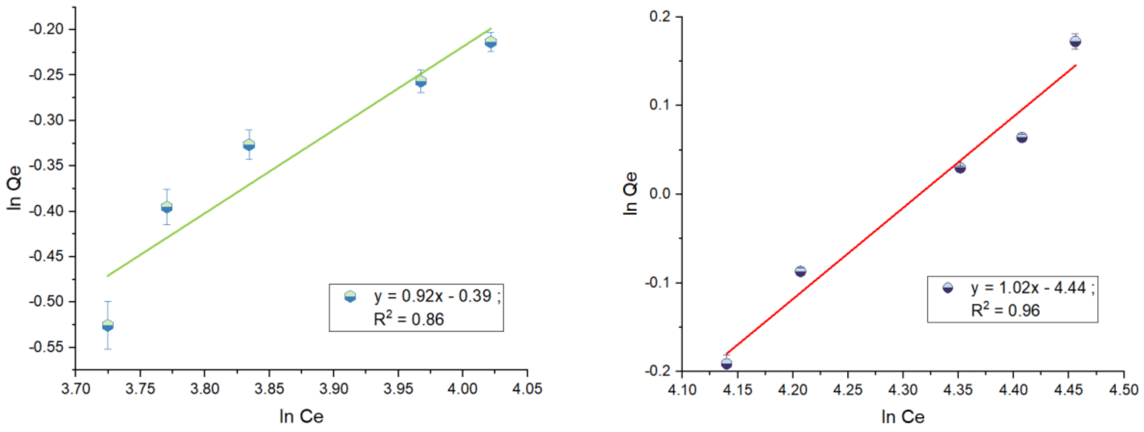
(d) Pb concentration: 1000 mg L^{-1}



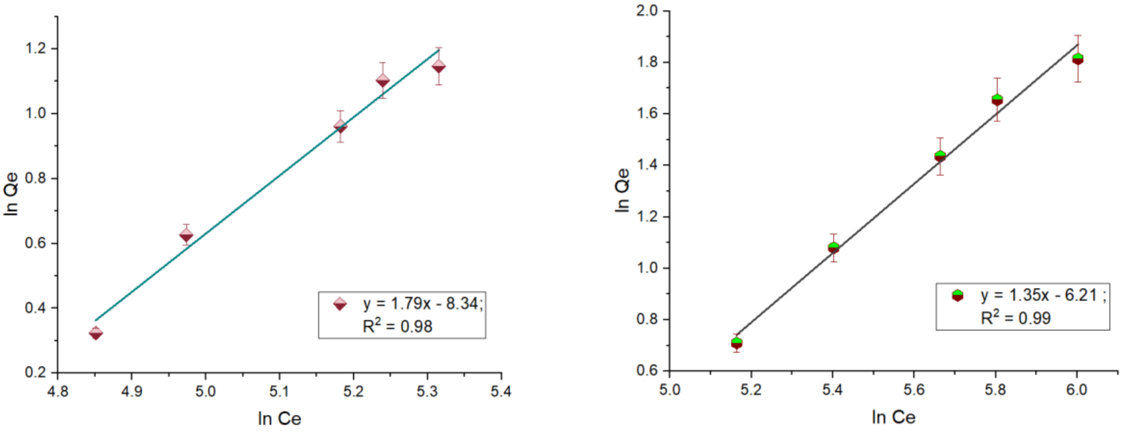
(e) Pb concentration: 1500 mg L^{-1}

(f) Pb concentration: 2000 mg L^{-1}

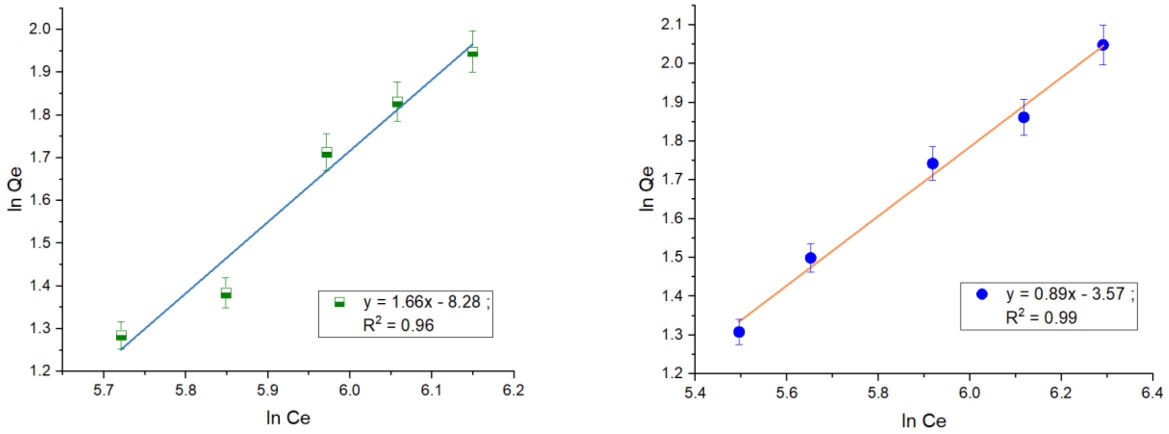
Figure 4. Freundlich Adsorption Isotherm for describing the effect of FYM in removing Pb as influenced by varying initial Pb concentrations. Bars represent standard error; data are average of two replications; comparison of mean was done at 5% level



(a) Pb concentration: 100 mg L^{-1} (b) Pb concentration: 250 mg L^{-1}



(c) Pb concentration: 500 mg L^{-1} (d) Pb concentration: 1000 mg L^{-1}



(e) Pb concentration: 1500 mg L^{-1} (f) Pb concentration: 2000 mg L^{-1}

Figure 5. Freundlich Adsorption Isotherm for describing the effect of coirpith in removing Pb as influenced by varying initial Pb concentrations. Bars represent standard error; data are average of two replications; comparison of mean was done at 5% level

4. Conclusion: This study establishes that both FYM and coirpith showed better Pb^{2+} sorption and removal potentials from aqueous solutions, however, FYM had higher Pb removal capacity than coirpith. The adsorption capacity increased with increasing Pb^{2+} concentrations at successive time intervals for both the sorbents. The models tested for sorbent-metal ion interactions showed that, both Langmuir and Freundlich models explained the Pb^{2+} adsorption mechanism well explaining that the monolayer coverage capacity (Q_m) increases with increasing Pb concentration while the binding affinity (K_L), adsorption capacity constant (K_F) and intensity of adsorbent (η) was higher for lesser initial Pb concentrations. Hence it could be concluded that, FYM is the effective sorbent used for removing Pb^{2+} from the contaminated aqueous systems.

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