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Lemon Juice and Microwave Assisted Modification of Potato Peel Husk for Lead Biosorption: Batch and Column Studies

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Abstract

The removal of heavy metals from water is very difficult. For this reason different methods have been employed so far among which biosorption is the cheapest and ecofriendly way to treat and remove heavy metals from aqueous media. Present study, investigated the ability of potato peel husk (PPH), potato peel husk modified with lemon juice (LMPPH) and potato peel husk modified with lemon juice & microwave (MLMPPH) for the removal of Pb (II) from water. Organic adsorbent was activated by lemon juice & microwave and was characterized by SEM, EDX and FTIR. Adsorption mechanism (batch parameters) and isothermal studies (Langmuir, Freundlich, Temkin isotherms) revealed the best fitness of Freundlich isotherm from the R² values indicating physisorption. Results of kinetic studies (pseudo first and second order and intraparticle diffusion) showed that reaction followed pseudo second order kinetics. In thermodynamic study reaction was exothermic (ΔH was negative). The ability of PPH, LMPPH and MLMPPH for removal of lead was also investigated in column studies (bed height, flow rate, influent concentration). Thomas Morrison adsorption model described breakthrough data. Recent study proved that activation of potato peel husk with lemon juice and microwave (MLMPPH) not only increased the sorption capacity of sorbent much more as compared to PPH and LMPPH due to the introduction of excess COOH groups with lemon juice but also their activation as COO⁻ with microwave exposure.

Keywords: Biosorption, PPH, Natural modification, SEM, EDX, Batch studies, Column studies.

Introduction

Shortage of potable water due to its rational use and its pollution due to heavy metals has become a serious problem nowadays. Different anthropogenic and natural sources are responsible for water pollution [1-4].

It is the need of the day to treat & control heavy metals sources to reduce these toxicants from the environment [5- 6] as they are nonbio-degradable and tend to accumulate causing various ill effects in living organisms [2, 7, 8].Various methods have been adopted for heavy metal removal from aqueous medium (electrochemical treatment, electrocoagulation, membrane filtration, ion exchange & photocatalytic process etc) [4, 9 - 12]. These methods are reported to be less

efficient and produce hazardous by products [1, 12-13].

To overcome these drawbacks adsorption is another method adopted for heavy metal removal from aqueous medium [11, 14 - 17]. Various biomaterials, industrial wastes, activated carbons, microorganisms, zeolites, nanomaterials, clay minerals can be selected as adsorbent [1, 8, 14, 18 - 20].

In addition to these methods, bio sorption by agricultural by products and plant wastes like rice husk ash [21], coconut shell [22], almond shell [23], tea waste [24], *Moringa oleifera* bark [25], wheat straw [26], banana peel [27] and mango peels [28] has become very popular because of their excess availability, low or no cost and high binding capacity for metals.

Agricultural wastes (lignin, cellulose, hemicellulose, extractives, lipids, proteins, sugars) are well known for their metal uptake capacity either in simple or in modified form. Biosorption by these agricultural wastes are attributed to the presence [29], activation and modification of various groups [30]. These groups like carboxyl, amide, amino, sulphonic when introduced or activated can enhance the adsorption power of adsorbent [31].

The biosorbents can be activated by using different chemicals like FeCl₃, ZnCl₂ [32], H₂O₂, H₂SO₄, NaOH [33- 34], citric acid, tartaric acid, HCl, HNO₃, KOH, acetone, ethanol, chloroform, polymerization, tetra ethylene glycol, diethyl ether, glycol [35, 36], urea [37] and thiourea [38]. Potato solanum tuberosum (family solanaceae) is the fourth largest crop in the world. There are 5000 varieties of potatoes worldwide. The potato peel is a waste and can be used as a biosorbent due to its abundance, easy availability, minute or no cost and its ability to uptake metal ions from aqueous solution. In this present research three types of biosorbents unmodified potato peel husk (PPH), modified potato peel husk with lemon juice (LMPPH) & microwave assisted lemon juice modified potato peel husk (MLMPPH) were used for the first time as a new biosorbent and its modification with lemon juice is totally ecofriendly instead of using various chemicals as modifiers or activators.

By adding lemon juice (ascorbic acid) there is the introduction of additional -COOH groups on adsorbent surface (potato peel) and with microwave radiation these groups are much more activated as COO⁻ providing more adsorbent sites for Pb (II) removal. This present research is totally eco-friendly using no chemicals and is economical by utilizing the agricultural waste.

The capability of unmodified PPH, LMPPH & MLMPPH of Pb (II) removal can be checked by studying isothermal, kinetic, batch & column studies.

Materials and Methods

HCl (0.1M), NaOH (0.1M), PbNO₃ (1M) were purchased from Sigma. FTIR spectrometer, shaker, pH meter, Microwave oven (2, 450 MHz), Atomic Absorption Spectrometer, SEM and EDX instruments were used for analysis and characterization.

Preparation of potato peel husk (PPH)

Potato peels (600 g) were converted to PPH when washed, dried, grinded and sieved (ASTM 60 mesh) to form husk and then stored in a jar for further experiments.

Preparation of lemon juice modified potato peel husk (LMPPH)

200 g PPH with lemon juice (1:2) were subjected to shaker at 100 rpm. After about 60 min. It is filtered and dried (75°C). This dried husk was LMPPH (lemon juice modified Potato Peel Husk).

Preparation of microwave lemon juice modified potato peel husk (MLMPPH)

PPH 200 g and lemon juice (1:1) were first irradiated with microwave radiation (2,450 MHz) for 20 min. It was then boiled (30 min) using double distilled water, filtered and again washed (20 mL hot double distilled water). This organic mass was then dried (50°C for 6 h) to get MLMPPH (Scheme 1).



Scheme 1: Surface modification of PPH with lemon juice & microwave activation

Preparation of lead nitrate solution

1 M standard lead nitrate solution and other working standards were made in double distilled water and their pH was adjusted with 0.1 M HCl and NaOH.

Results and Discussion *FTIR Analysis*

FTIR analysis of PPH, LMPPH and MLMPPH showed different functional groups before and after activation Fig. 1. In case of LMPPH an additional peak in the region of 694.37 cm⁻¹ showed the presence of triple bond (alkynes) which was not present in PPH. LMPPH showed additional carboxylic acid peaks with OH in the region of 1751.36 cm⁻¹ and 972.12 cm⁻¹. This peak 972.12 cm⁻¹ was shifted to 979.84 cm⁻¹after microwave activation of LMPPH. Peak at 1597.06 cm⁻¹ was due to aromatics with C-C stretch and at 2314.58 cm⁻¹ with C triple bond N stretch which only appeared in MLMPPH. Peak at 1049.28 cm⁻¹ is of C-N stretching in PPH and LMPPH which was shifted to 1056.99 cm⁻¹ in case of MLMPPH. Peak of 1651.07 cm⁻¹ showed presence of C=O on the surface of PPH and after microwave activation of LMPPH it was shifted to 1674.21 cm⁻¹. Carboxylate ion peak were at 1512.19 cm⁻¹ 1342.46 cm⁻¹, 1273.02 cm⁻¹ and 1172.72 cm⁻¹ [39]. The presence of all these groups were responsible for chelation of cations from water.



Figure 1. Over lay FTIR spectra of MLMPPH (1), PPH (2), LMPPH (3)

SEM analysis

SEM image of PPH showed the surface of

PPH as porous and rough. After lemon juice treatment its surface become more porous (LMPPH) having small opening with wavy edges. After microwave treatment MLMPPH particles was not only porous, irregular with wavy edges but also have very small size thus providing large surface for binding with metal ions than PPH and LMPPH Fig. 2a-c. Thus treatment and modification with lemon juice and microwave radiation boosted the binding capacity of PPH [40- 41] and in turn the biosorption.



Figure 2a. SEM image of the surface PPH



Figure 2b. SEM image of the surface LMPPH



Figure 2c. SEM image of the surface MLMPPH

EDX analysis

EDX image of PPH shows its elemental composition as having Ca, K, Na and no Pb but for MLMPPH an additional prominent peak is observed due to retention of lead on the surface of biosorbent Fig. 3a-b.



Figure 3a. EDX image of Pure PPH without lead



Figure 3b. EDX image of MLMPPH with lead

Batch study with PPH, LMPPH & MLMPPH Shaking speed

To study the ability of PPH, LMPPH & MLMPPH against Pb (II) removal different

shaking speeds (50, 100-450 rpm for 30 min was set with sorbate concentration of 25 ppm/50 mL. It was observed that 100 rpm shaking speed was best for PPH & MLMPPH and 150 rpm for LMPPH having removal percentage of 83 %, 85 % and 94 % for PPH, LMPPH and MLMPPH, respectively. At moderate speed adsorbent was distributed throughout providing more active sites. At low shaking most of it was settled at the bottom resulting in concealment of layers and hence less interaction. While with high speed kinetic energies of ions (Pb^{+2}) and adsorbent was increased resulting in less interaction between each other Fig. 4a.



Figure 4a. Effect of shaking speed for lead removal onto PPH, LMPPH and MLMPPH. Adsorbent dose = 0.3 g, Shaking speed (RPPH) = 100 rpm, Solution concentration (25 ppm / 50 mL), Contact time = 30 min

Contact Time

The removal efficiency of PPH, LMPPH and MLMPPH for different contact times (5, 10, 15-70 min) were taken. After 60 min time interval maximum removal efficiency (%) for PPH was 87 % and for LMPPH was 89 % and after only 30 min for MLMPPH removal was 96 % Fig. 4b.



Figure 4b. Effect of contact time for lead removal onto PPH, LMPPH and MLMPPH. Adsorbent dose = 0.3 g, Shaking speed (PPH, MLMPPH) = 100 rpm, Shaking speed (LMPPH) = 150 rpm, Solution concentration (25 ppm / 50 mL), Temperature = 293 K

Mass of Adsorbent

Maximum adsorption of Pb (II) was done with 0.5 g for PPH, 0.3 g of LMPPH and only 0.1 g with MLMPPH. Removal capacity of all the three sorbents (PPH, LMPPH, MLMPPH) had increased with the increasing amount of adsorbent and after reaching equilibrium adsorption decreased due to their aggregation and less interaction Fig. 4c.



Figure 4c. Effect of adsorbent dose (g) on lead removal onto PPH, LMPPH and MLMPPH. Shaking speed (PPH, MLMPPH) = 100 rpm, Shaking speed (LMPPH) = 150 rpm, Solution concentration (25 ppm / 50 mL), Time = 30 min, Temperature = 293 K

pH dependence

To study the effect of pH on sorption by PPH, LMPPH and MLMPPH pH from 3 to 11 was set. Results indicated that MLMPPH and LMPPH had more capability to adsorb Pb (II) than the PPH Fig. 4d.



Figure 4d. Effect of pH on lead removal onto PPH, LMPPH and MLMPPH. Adsorbent dose (PPH, LMPPH, MLMPPH) = 0.3 g, Shaking speed (PPH, MLMPPH) = 100 rpm, Shaking speed (LMPPH) = 150 rpm, Solution concentration (25 ppm / 50m L), temperature = 293 K, Time=30 min

Acidic conditions are favorable for metal uptake as there is an increase in affinity of potato peels to metal ions. Ionic state of functional group is pH dependent. PPH mainly has hydroxyl groups where as in LMPPH and MLMPPH there are additional -COOH groups. At low pH (less than 3) non-ionic –COOH is present and hence less Pb⁺²adsorption. Whereas, when pH is 5 the main specie is -COO⁻ and hence due to electrostatic interaction Pb⁺²adsorption is high. At pH 5 there was maximum removal efficiency (%) of MLMPPH 96 % and 95 % for LMPPH and at pH 4 was 92 % for PPH.

At higher pH about 6.0 there was the precipitation of Pb^{+2} as Pb (OH)₂.

$$2PP-OH + Pb^{+2} \longrightarrow (PPO)_2 Pb^{+2} + 2H^+ (PPH)$$
$$PPLM^{-2} + Pb^{+2} \longrightarrow PPLM- Pb (LMPPH)$$

Temperature dependence

Temperature is one of the major factor to study the phenomenon of adsorption on PPH, LMPPH & MLMPPH (283 K - 323 K) Fig. 4e. It was observed that 293 K was the more favorable temperature and removal efficiencies (%) were 91 %, 91 % and 93 % for PPH, LMPPH and MLMPPH. After 293.0 K there was decrease in removal efficiency due to increased motion and less time of interaction between sorbent and sorbate.



Figure 4e. Effect of temperature (K) on lead removal onto PPH, LMPPH and MLMPPH. Adsorbent dose = 0.3 g, Shaking speed (PPH, MLMPPH) = 100 rpm, Shaking speed (LMPPH) = 150rpm, Solution concentration (25 ppm / 50mL), Time = 30 min

Thermodynamic parameters including ΔG° (standard free energy), ΔH° (standard enthalpy) and ΔS° (standard entropy) were calculated Table 1 using the equation to study the adsorption behavior of the adsorbents.

 $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$

 $\Delta G^{\circ} = - RT \ln KD$

$$Kd = \frac{q_e}{C_e}$$

The negative ΔG values for PPH, LMPPH and MLMPPH indicated the spontaneity and feasibility of reaction. Greater value of ΔG was for MLMPPH which means that adsorption was more favorable with MLMPPH as compared to LMPPH and PPH. Negative value of ΔH means exothermic nature of reaction. Positive ΔS value means randomness of binding sites. Among the adsorbents PPH had more ΔS value.

Table 1. Thermodynamic parameters for adsorption of lead onto PPH, LMPPH, MLMPPH.

Adsorbent	Temperature	ΔG°	ΔH°	ΔS°
РРН	283	-11.447	-11.37	0.31
	293	-11.274		
	303	-12.579		
	313	-13.345		
	323	-14.154		
	283	-11.749	-10.78	0.23
LMPPH	293	-11.005		
	303	-11.950		
	313	-13.345		
	323	-14.154		
	283	-10.630	-10.25	0.21
MLMPPH	293	-10.749		
	303	-11.659		
	313	-12.661		
	323	-13.409		

Isothermal study

Langmuir isotherm

Langmuir parametrs including q_{max} (maximum sorption capacities), R_L (separation factor) and R^2 (regression coefficient) were calculated from Langmuir isotherm for PPH, LMPPH and MLMPPH (Table 2) using equations.

Table 2. Isothermal parameters for lead sorption onto PPH, LMPPH and MLMPPH.

Adsorbent	Langmuir		Freu	Freundlich		Temkin	
РРН	$q_{max}(mg/g)$	4.992	n	0.272	B _T	0.030	
	b (L/g)	9.363	K_F	1.732	K _T	1.342	
	\mathbb{R}^2	0.991	\mathbb{R}^2	0.956	\mathbb{R}^2	0.774	
	R _L	0.004	1/n	3.669	lnkt	0.294	
LMPPH	q _{max} (mg/g)	5.652	n	0.248	BT	0.025	
	b (L/g)	15.982	K_F	4.549	K _T	1.073	
	\mathbf{R}^2	0.994	\mathbb{R}^2	0.966	\mathbb{R}^2	0.752	
	R _L	0.002	1/n	4.017	lnkt	0.070	
MLMPPH	q _{max} (mg/g)	8.710	n	0.333	BT	0.029	
	b (L/g)	31.768	K_F	5.620	K _T	1.013	
	\mathbf{R}^2	0.894	\mathbb{R}^2	0.989	\mathbb{R}^2	0.889	
	R _L	0.001	1/n	2.997	lnkt	0.013	

Note: q max = maximum monolayer adsorption capacity (mg/g); b = Langmuir constant related to energy of adsorption; qe = adsorption capacity (mg of adsorbate per gram of adsorbent); KF = relative adsorption capacity; n = adsorption intensity; BT and KT are Temkin constant

$$qe = \frac{qmax \ b \ Ce}{1+b \ Ce}$$

(q_e is adsorption capacity in mg, q_{max} is monolayer adsorption capacity of adsorbent mg g⁻¹, b is Langmuir constant related to energy of adsorption, C_e is concentration of adsorbate mg L⁻¹. Factor b was used to calculate equilibrium parameter R_L which explains the favorability of the reaction.

$$\mathrm{RL}=\frac{1}{1+b\ Ce}$$

MLMPPH had greater qmax value (8.710 mg.g⁻¹) which is the indication of greater number of active sites than LMPPH (5.652 mg.g⁻¹) and PPH (4.992 mg.g⁻¹). R_L value of PPH, LMPPH and MLMPPH (0.004, 0.002 and 0.001) is an indication that reaction was favorable but non-linearity of graphs (1, 2) and low R^2 values did not satisfy Langmuir isotherms Fig. 5a-b.



Figure 5a. Langmuir 1 isotherm for PPH, LMPPH, MLMPPH



Figure 5b. Langmuir 2 isotherm for PPH, LMPPH, MLMPPH

Frendulich isotherm

Freundlich model explains multilayer adsorption of metal ions on the heterogeneous surface mainly due to physiosorption mode [42]. The values of n (adsorption intensity), K_F (adsorption capacity) and R^2 (coefficient of determination) were calculated from Freundlich isotherm. Freundlich equation is:

$qe = KF Ce^{1/n}$

(q_e adsorption capacity (mg of adsorbate per gram of adsorbent), K_F relative adsorption capacity, n adsorption intensity, C_e concentration of solution).

The value of n increases from PPH, LMPPH and MLMPPH i.e. 0.272, 0.248 and 0.333 Table 2. The K_F increases from PPH, LMPPH and MLMPPH from 1.732 mg/g, 4.549 mg/g, 5.620 mg/g because after modification of PPH with lemon juice adsorptive capacity had increased. The linear graph of Freundlich adsorption isotherm and R^2 values greater than 0.99 (Rsquared is a statistical measure of how close the data are to the fitted regression line) is according to Frendulich and is an indication of physisorption [42] Fig. 5c.



Figure 5c. Freundlich isotherm for PPH, LMPPH, MLMPPH

Temkin isotherm

Temkin adsorption isotherms were used to study the extent of sorption. The values of KT& BT were calculated Table 2. Temkin equation is:

$qe = BT \ln KT Ce$

(B_T and K_T are Temkin constants, C_e is concentration of solution) KT (adsorption capacity) values for PPH, LMPPH and MLMPPH were 1.342 mg/g, 1.073 mg/g and 1.013 mg/g, respectively. B_T (Heat of adsorption value less than 8 is an indication of weak interaction) for PPH, LMPPH and MLMPPH were 0.031 KJ/mol, 0.025 KJ/mol and 0.029 KJ/mol. B_T value lower than 8 indicated physiosorption, (weak interaction) and value more than 8 indicated chemisorption during metal ion removal [41]. Here the results of isothermal studies showed physiosorption mode. Temkin isotherm did not hold good for this reaction Fig 5d.



Figure 5d. Temkin isotherm for lead removal onto PPH, LMPPH, MLMPPH

Kinetic study

In order to determine the sorption rates and possible reaction mechanism pseudo first order, pseudo second order and intraparticle diffusion model were investigated.

Pseudo first order parameters were calculated by:

$$\frac{dqt}{dt} - kl(qe - qt)$$

Ln (qe-qt) = lnqe - k1t

(where qt is the amount of lead ions removed at time t (mg/g), q_e is the adsorption capacity at equilibrium (mg/g), k_1 is the pseudo-first-order rate constant (1/min), and t is the contact time (min).

Pseudo second order parameters were calculated by:

$$\frac{\mathrm{d}qt}{\mathrm{d}t} - \mathrm{K2}(\mathrm{qe} - \mathrm{qt})^2$$
$$\frac{\mathrm{t}}{\mathrm{qt}} = \frac{1}{\mathrm{k2} \mathrm{qe}^2} + \frac{\mathrm{t}}{\mathrm{qe}}$$

The relation between the experimental qe and calculated qe value is given by R^2 values. For pseudo first order the rate constant K_1 and difference in qe (exp) and qe (cal) indicated lower R^2 values (Table 3) for PPH, LMPPH and MLMPPH which did not fit pseudo-first order model Fig. 6a. For pseudo second order the values of K_2 and qe (exp) and qe (cal) were in good agreement with each other for the three adsorbents Table 3 thus the sorption is according to pseudosecond order kinetics Fig 6b as the R^2 values for PPH, LMPPH and MLMPPH were close to unity [43].



 $Figure \ 6a.$ Pseudo first order kinetics for adsorption of lead onto PPH, LMPPH, MLMPPH



Figure 6b. Pseudo-second order kinetic model for sorption data of lead onto PPH, LMPPH, MLMPPH

Intra particle diffusion

The intraparticle diffusion model describes adsorption processes, where the rate of adsorption depends on the speed at which adsorbate diffuses towards adsorbent (i.e., the process is diffusion-controlled), which is presented by equation:

$$qt = kidt^{\frac{1}{2}} + C$$

(kid (mg/g min) = intraparticle diffusion rate constant, C (mg/g)= constant proportional to the extent of boundary wall thickness). The values of these parameters were calculated for PPH, LMPPH and MLMPPH Table 3.

Table 3. Kinetic parameter for lead adsorption using PPH, LMPPH and MLMPPH.

Kinetic Parameters		PPH	LMPPH	MLMPPH
	\mathbb{R}^2	0.984	0.998	0.999
Pseudo second order	K_2 (min ⁻¹)	0.215	1.564	0.259
	qe (mg/g) (cal)	3.347	3.582	3.743
	qe (mg/g) (exp)	3.64	3.71	4.0
Pseudo first order	\mathbb{R}^2	0.462	0.368	0.614
	K ₁ (min. ⁻¹)	0.0008	0.0001	0.0003
	lnqe	2.524	2.467	2.429
	qe (mg/g)	12.489	11.795	11.349
Intraparticle diffusion model	K _{id} (mg/g min)	0.111	0.003	0.030
	C (mg/g)	2.586	3.576	4.061

Note: qe (mg/g) = sorption capacity at equilibrium; K1 (L/min) = rate constant of pseudo first order adsorption; K2 = rate constant for pseudo second order reaction; kid (mg/g min) = intraparticle diffusion rate constant.

In intra particle diffusion model for PPH a nonlinear line not passing through the origin is an indication of the nonavailability of active sites and hence no adsorption. A linear graph is obtained for LMPPH and MLMPPH as compared to the PPH which means availability of active sites and hence adsorption Fig 7.

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Figure 7. Intraparticle diffusion for adsorption of lead onto PPH, LMPPH, MLMPPH

Column experiment and Thomas kinetic model

The data obtained from batch conditions were not applicable to column studies where contact time was not sufficiently long enough for the attainment of equilibrium. So to study adsorption kinetics in a column Thomas model has been used [44-45]. The Thomas model is described by equation:

$$\frac{Cs}{Co} = \frac{1}{1 + sxp[\frac{K}{Q} (qoM - CoV)]}$$

(Ce = effluent solute concentration (mgL^{-1}) Co = Influent solute concentration $(mg.L^{-1})$ K = Thomas rate constant $(mLmin^{-1}. mg^{-1})$ qo = maximum solid phase concentration of solute mg.g⁻¹) M = mass of sorbent (g) V = throughput volume (mL) Q = volumetric flow rate $(mLmin^{-1})$. Thomas equation was linear and is fitted to the breakthrough data to calculate value of k and qo.

The linearized form of Thomas equation used is:

$$ln \left(\frac{Co}{Ce} - 1\right) = \frac{k \ qo \ M}{Q} - \frac{k \ Co \ V}{Q}$$

Column studies can be studied by plotting breakthrough curves (between Ce/Co against time). The kinetic coefficient KT and the adsorption capacity of the bed qo were determined from the plot. Different amount of biomasses PPH, LMPPH and MLMPPH (6g, 10g) were packed. The results of KT, R^2 and qo were given in Table 4. Values of regression coefficients were determined which showed a good fit of the Thomas Kinetic Model. The sorption capacity of PPH, LMPPH & MLMPPH vary from 2.713×10^{-07} – 5.376×10^{-09} mg/g Table 4. This decrease in value

was due to shortage of Pb (II) in solution as compared to sorbent amount. Less sharp curves indicate less mass transfer rate and diffused and Sshape curves showed infinite mass transfer rate.

Table 4. Thomas model equation for adsorption of lead onto PPH, LMPPH, MLMPPH for different amount of biomass packed.

Amount of biomasses packed(g)	\mathbf{R}^2	K _T = Intercept/C _o	q ₀ (mg/g)
PPH 6 g	0.862	0.002	$2.713\times10^{\text{-}07}$
LMPPH 6 g	0.939	0.001	$2.036\times 10^{\text{-}07}$
MLMPPH 6 g	0.965	0.001	$1.573\times 10^{\text{-}07}$
PPH 10 g	0.982	0.0001	$4.612\times10^{\text{-08}}$
LMPPH 10 g	0.949	0.00001	$5.376 \times 10^{\text{-09}}$
MLMPPH 10 g	0.977	0.0001	$4.261\times10^{\text{-08}}$

Effect of bed Height

Different sorbents (PPH, LMPPH and MLMPPH) were used for column bed with increasing bed height from 6 cm to10 cm. Sorption has increased with increasing bed height Fig. 8a due to increased surface area of biosorbent. The breakthrough time was also increased with the increase in bed height [46].





Effect of concentration of sorbate

Metal ion uptake is decreased with the increasing concentration of sorbate. It showed that increase in concentration of lead (40 ppm) decreases the sorbent metal ratio and hence the uptake of metal Fig. 8b. The biosorbent got saturated earlier and the breakthrough time decreased.



Figure 8b. Breakthrough curves for lead adsorption by PPH, LMPPH, MLMPPH packed bed with different influent concentration. Average flow rate 6 mL/min, influent lead concentration (20-40 ppm), biomass packed 10 g.

Effect of flow rate

Adsorption highly depends on flow rate. When there was high flow rate of 12 mL/min⁻¹ adsorption of lead was decreased due to less time of interaction Fig. 8c. Another reason is that the biosorbent got saturated earlier and the breakthrough capacity of biosorbent was decreased.



Figure 8c. Breakthrough curves for lead adsorption by PPH, LMPPH, MLMPPH packed bed with different influent flow rate, influent lead concentration (20 ppm), biomass packed 10 g.

Conclusion

It is concluded on the basis of results that PPH, LMPPH and MLMPPH could be successfully used for the removal of lead from aqueous media. MLMPPH adsorbent, prepared by lemon juice & microwave assisted method offers highest adsorption capacity for removal of Pb (II)

from aqueous solution as compared to PPH and LMPPH. The surface of MLMPPH has more active sites and that's why it shows highest sorption capacity. Batch and column experiment were conducted and absorption was noted by AAS. Batch experiment was best for removal of lead from aqueous media. Adsorption process was illustrated by pseudo second order kinetics model. Adsorption data was fitted extremely well to the Freundlich isotherm. Thermodynamic calculations revealed that lead adsorption process by PPH, LMPPH and MLMPPH has exothermic nature. The results proved that the MLMPPH has greater sorption capacity for the removal of lead due to presence of COO⁻ group on the surface. It could be used for sorption of different other heavy metals like Cd, As etc. and also for different dyes such as methylene blue etc. from water. Activation by lemon juice is very effective, low cost and at the end of reaction sludge or by products is not formed. This method is easily applicable in agricultural country where a lot of agricultural waste is present and lemon juice is also abundantly available. This method can be applied on industrial scale to remove contaminants from waste water.

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