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Research Paper

A Study On The Competitive Removal Of Pb(II) In The Presence Of Ni(II) Using Thiolated Rice Husk Through Equilibrium, Kinetic And Thermodynamic Modelling

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Abstract: *In the quest for finding effective adsorbents for metals, the present study is focused on the removal of Pb(II) ions from aqueous solution using thiolated rice husk by batch and column studies. The presence of metals as a single component in waste waters is highly unlikely, the effect of Ni(II) on the removal of Pb(II) from mixtures of Pb(II)+Ni(II) ions has been investigated. Thioglycolic acid has been used for thiolation of rice husk. The adsorbent has been characterized using proximate and FTIR analyses. Maximum adsorption obtained by batch studies is 93% at pH 5, metal ion concentration 300mg/L in 150mins for 212 micron size at 298K. Isotherm analyses show that both Langmuir and Freundlich isotherm models are best obeyed. The process is endothermic and spontaneous in nature and follows pseudo first order kinetics and intraparticle diffusion also occurs but is not the rate determining step. Application of Langmuir competitive model for the binary sorption system shows that adsorption of Pb(II) has been supressed by presence of Ni(II) ions. Breakthrough curve analyses of data from sequential bed as well as vertical bed columns at varying inlet concentrations and flow rates suggest that the adsorbent is effective and can find industrial applicability.*

Keywords: Binary adsorption, Thiolated rice husk, Isotherm analysis, Kinetic study, Thermodynamic parameters.

Introduction

Heavy metals due to their widespread use in industry are the most common pollutants of the aquatic ecosystem and industrial waste with significant amount of heavy metal ions is discharges into the aquatic environment1. Water contamination is a matter of concern, globally[2,3]. Presence of heavy metal ions in surface water causes toxicity to aquatic, animal and human life, even at very low concentrations. Lead is found to be the most detectable metal ion in waste water effluents as a large number of industries[4,5]. Lead is highly toxic also prevents the production of haemoglobin in the body6. The permissible limit for Pb(II) in waste water is 0.05-0.1mgL^{-1} and in drinking water the safe limit specified by various agencies is 0.010-0.015mgL^{-1} [4]. It is therefore, essential to remove Pb(II) from wastewater before disposal. A number of techniques have been developed for the removal of Pb(II) but the adsorption process offers significant advantages due to its simplicity, high efficiency, easy metal recovery and possibility of regeneration of adsorbent in industrial applications[3]. Agricultural based residues as adsorbents are of considerable interest for the removal of metal ions from waste water, as hemicelluloses, lignin or hydrocarbons present in agricultural based materials can easily bind the metal cations from aqueous solutions3.However, studies reveal that chemically modified agricultural wastes are more effective for the removal of heavy metal ions from waste water than unmodified agricultural wastes[7]. Therefore, it was thought worthwhile to study the adsorption potential and selectivity of thiolated rice husk for the removal of Pb(II) ions from aqueous solution. Since metals are generally not present as a single component in waste waters and few literature reports are available on the competitive removal of metals[8,9], it was thought worthwhile to study the effect of the presence of Ni(II) on the adsorption of lead from binary metal system of Pb(II)+Ni(II) ions as there may exist some mutual interferences and competition between two or more components for the adsorption sites.

Materials and Methods

Preparation of the Adsorbent

Rice (*Oryza sativa*) husk (variety PR 106) was procured from agricultural land of Sangrur, Punjab, India. Thiolation of rice husk was carried out using reported method[10] by treating it with 0.1 M thioglycolic acid in a round bottomed flask fitted with a condenser and continuously stirred for 24 hr at 25º-30ºC. The mixture was filtered and thiolated material was washed with distilled water and then dried at 80°C.

Preparation of Adsorbate Solution

Stock solution of concentration 300 mg/L and working standard solutions (i.e 30-300mg/L) of Pb(II) ions were prepared in distilled water using $PbCl_2$ (Merck, A.R grade). Binary solution for (Pb+Ni) system were obtained by varying the concentration ratios of Pb(II) + Ni(II) in the range 1:0, 1:1, 1:2,1:3 and 1:4 for fixed Pb(II) ion concentration of 30mg/L, 60 mg/L and 90 mg/L[11].

Characterisation of Adsorbent

Proximate analysis

Proximate analysis was carried out by heating 5gms of the sample at 100°C for 1 hour to get the moisture content and further heating upto 700°C to determine the ash content.

Fourier Transform Infrared Spectroscopy (FTIR) analysis

FTIR Spectra using Nicolet impact equipment with detector at resolution of 4 cm^{-1}. were recorded as KBr pellets (i.e mixture of 1mg powdered adsorbent with 100 mg KBr). The intensities of absorption bands were recorded for 32 scans per sample in the scanning range of 500 to 4000 cm^{-1}.

Degree of Thiolation

The degree of thiolation was determined by the reported method[10] by treating 0.5g of thiolated rice husk with excess of 0.5M- iodine solution and the unreacted iodine was back titrated with 0.1 M sodium thiosulphate using starch as indicator. The degree of thiolation was calculated from the titre values.

$$T = \frac{(V - V')}{W} \times M$$

where T = degree of thiolation; V = volume (ml) of 0.1M-$Na_2S_2O_3$ solution used in blank titration; V′ = volume (ml) of 0.1M $Na_2S_2O_3$ used for titration of solution with 0.5g thiolated rice husk used; W = sample weight(0.5g) M = Molarity of $Na_2S_2O_3$ used.

Batch Adsorption Studies

A known weight of adsorbent (250mg) was added in 10ml of metal ion solutions (300 mg/L to 30mg/L concentration) for regular time intervals varying from 30 to 180mins. (till equilibrium) at varying pH (2-8), adjusted by the addition of hydrochloric acid or ammonium chloride and ammonium hydroxide depending upon the pH desired. The resultant solutions were filtered and analysed for metal ion concentration in single as well as binary metal solution. The metal concentration was determined titrimetrically[12,13], using standard EDTA solution.

Column Studies

Continuous flow column studies using sequential bed column and vertical bed columns have been carried out.

(i) Sequential bed column – The sequential bed column was constructed by connecting glass tubes of 1.5cm diameter to hold the adsorbent without using other materials and the solution was allowed to flow under gravity. The first tube, filled with solid adsorbent, received the influent (controlled by a valve) which flowed through the second tube and so on.

(ii) Vertical column – A vertical column of 4 cm diameter and 60 cm height containing the adsorbent was set up. The down flow mode has been used and the flow through the column was maintained using a rotameter to measure the flow. The adsorbent was packed up to a depth of 40 cm in the column.

Results and discussion

Characterisation of Adsorbent

Proximate analysis and Degree of Thiolation

The moisture content at 100°C was found to be 5% and ash content at 700°C was 40.3%. The amount of silica in rice husk was determined gravimetrically[10] and was found to be 12%. The degree of thiolation for thiolated rice husk was found to be 2.8.

Fourier Transform Infrared Spectroscopy (FTIR) analysis

Infrared spectrum of thiolated rice husk shows similar bands as in FTIR spectra of rice husk[12] bands at 3419cm^{-1} attributed to the surface hydroxyl groups and chemisorbed water, 2926cm^{-1} to symmetric or asymmetric C–H and the symmetric stretching vibration of CH_2. A band at 1651cm^{-1} is indicative of stretching vibration of C–O bonds due to non-ionic carboxyl groups (–COOH, –$COOCH_3$) and between 1020 to 1158cm^{-1} is indicative of SO_3 stretching in addition peaks are observed between 1000 to 1350cm^{-1} assigned to O–H of alcohol and aliphatic ethers and peak at 800cm^{-1} is indicative of sulphur functional (-SH) groups.

Effect of initial metal ion concentration and contact time

Amount of metal ion adsorbed increases but percentage removal decreases with increase in initial metal ion concentration in the range 30-300mg/L at 298K. At low concentration, the ratio of Pb(II) ions to the number of available adsorption site is low hence higher adsorption. Maximum removal takes place in the initial 30 minutes and equilibrium is attained at 150min., which is explained on the basis that number of adsorption sites decreases with time[11,13].

Effect of pH

The effect of pH has been studied in the pH range 2-8 (beyond pH 8 precipitation of Pb(II) ions occurs)[3], for initial metal ion concentration 300mg/L at contact time of 150min. at 298K, amount of Pb(II) adsorbed increases with pH from 2 to 5, further increase in pH shows a decline in amount adsorbed (Fig.1). At low pH due to higher concentration of H^+ ions there is a competition with positively charged Pb(II) ions[16,17]. With increase in pH the competitive effect of H^+ ions decreases and adsorption increases. Further increase in pH shows a decrease in the amount of Pb(II) adsorbed due to the formation of soluble or insoluble $Pb(OH)_2$.

Effect of particle size

Studies with adsorbent particles of sizes 212, 425 and 600 microns have been used at pH 5 for metal ion concentration 300 mg/L and contact time of 150 mins, the experimental data shows that amount of Pb(II) adsorbed decreases with increase in particle size, which is due to availability of more surface area for smaller particle size adsorbent. The percentage removal is 93.3% for 212 micron size particle, which decreases to 80.2% for 425 micron and further to 72.4% for 600 micron size particle of the adsorbent.

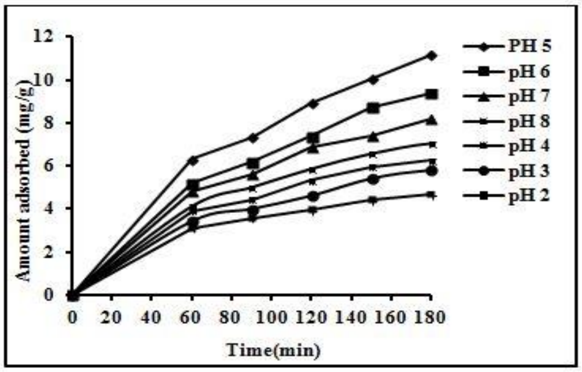

Figure 1: Amount of Pb(II) adsorbed on thiolated rice husk at different pH vs time on particle size 212 micron at metal ion concentration of 300mg/L

Adsorption Isotherm Studies

The data obtained for adsorption at pH 5 and contact time of 150 minutes, adsorbent particle size 212 micron and metal concentration range 30-300 mg/L have been subjected to various adsorption isotherm models. The parameters were obtained through the equilibrium isotherm model adjustment. These parameters give information about the adsorbent/adsorbate affinity and adsorbent surface properties, which helps to comprehend the adsorption mechanism.

Freundlich isotherm

The Freundlich equation can be given as:

$$\log q_e = \log K_f + {}^{1}\!/_{n} \log C_e \tag{1}$$

where C_e is the equilibrium metal ion concentration (mg/L) and q_e is the amount adsorbed at equilibrium time(mg/g). The values of n and K, determined from slope and intercept of the straight line plot of log q_e vs. log C_e are given in Table 1. The value of $1<n<10$ indicates the effectiveness of the adsorbent and high R^2 value of 0.997 suggests favorable and monolayer adsorption[11,18].

Langmuir adsorption isotherm

Langmuir equation is given as:

$$C_e/q_e = 1/bQ_m + \left(1/Q_m\right) C_e \tag{2}$$

where C_e is the equilibrium metal ion concentration (mgL^{-1}), q_e is the amount of adsorbate adsorbed at equilibrium time for unit weight of adsorbent (mgg^{-1}), b is adsorption equilibrium constant related to apparent energy of adsorption (Lmg^{-1}) and Q_m maximum adsorption capacity (mg/g). The values of Q_m and b, as obtained from a plot of C_e/q_e against C_e are given in Table 1. Results suggest homogenous monolayer adsorption on the surface[11] with maximum adsorption capacity of 7.50 mg/g.

A further analysis of Langmuir equation is made on the basis of R_L also known as separation factor,

$$R_L = 1/(1 + a_L\, C_o) \tag{3}$$

where C_0 is the initial metal ion concentration, R_L is separation factor. The values of R_L have been found to be 0.018 (between 0 and 1), suggests favorable adsorption[11].

Temkin isotherm

The linearised form of Temkin equation is:

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{4}$$

Where, q_e is the equilibrium adsorption capacity (mg/g), B_T is constant related to heat of adsorption (J/mol), T is absolute temperature (K) and R is universal gas constant, 8.314 J mol^{-1} K^{-1} [11]. The values of the isotherm constants A_T and B_T obtained from the slope and intercept of plot of q_e vs. ln C_e (Table 1), the value of R^2 value of 0.942 indicates that the Temkin isotherm fitted the data but the level of fitness was lesser than that of the Langmuir model and the Freundlich model.

Dubinin-Radushkevitch (D-R) isotherm

Dubinin-Radushkevitch isotherm is given as follow:

$$\ln q_e = \ln Q_m - K\,\varepsilon^2 \qquad (5)$$

where K($mol^2\ kJ^{-2}$) is a constant related to adsorption energy, Q_m($mg\ g^{-1}$) is the maximum adsorption capacity, The Polanyi potential ε can be expressed as:

$$\varepsilon = RT \ln (1 + 1/C_e) \qquad (6)$$

Where R is universal gas constant, 8.314 J $mol^{-1}K^{-1}$, T is absolute temperature (K) and C_e is the drug equilibrium concentration (mgL^{-1}) [11].

The values of K and Q_m are calculated from the plot of ln q_e and ε^2. Adsorption parameters are given in Table 1. The value of correlation coefficient 0.963, suggests the applicability of D-R isotherm model. Using the value of K, the mean sorption energy E (kJ mol^{-1}) can be evaluated from,

$$E = K^{-1/2} \qquad (7)$$

Value of E is 1.88 lies b/w 1-16 kJ mol^{-1} indicates that physical adsorption is taking place.

Table 1: Adsorption isotherm constants for adsorption of Pb(II) ions on thiolated rice husk for varying metal ions concentrations at 298 K and pH-5

Metal ion	Freundlich			Langmuir			Temkin				D-R			
Mn(II)	n	K_f (mg/g)	R^2	Q_m (mg/g)	b (L/mg)	R^2	A_T (L/g)	B_T (J/mol)	b_T	R^2	K (mol^2/kJ^2)	Q_m (mg/g)	E (kJ/mol)	R^2
	0.03	1.02	0.991	7.50	1.80	0.952	54.4	3.19	776.6	0.942	0.37	22.4	1.16	0.96

Error Analysis for Isotherm Studies

To optimise the best fit of isotherm equations to the experimental data, five different error functions of non-linear regression can be used for the evaluation of errors in isotherm curves.

Sum of squared errors (SSE):

$$SSE = \sum_{i=1}^{n} (q_{e,cal} - q_{e,exp})^2 \qquad (8)$$

Sum of absolute errors (SAE):

$$SAE = \sum_{i=1}^{n} \left| q_{e,cal} - q_{e,exp} \right|_i \qquad (9)$$

Average relative error (ARE):

$$ARE = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{q_{e,cal} - q_{e,exp}}{q_{e,exp}} \right| \qquad (10)$$

Hybrid fractional error function:

$$HYBRID = \sum_{i=1}^{n} \left[\frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,exp}} \right]_i \qquad (11)$$

Marquardt's percent standard deviation (MPDS):

$$MPSD = \sum_{i=1}^{n} \left[\frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right]^2 \qquad (12)$$

The value of $q_{e,cal}$ for all isotherm models and the values of the five error functions are shown in Table 2. The analyses suggest that Freundlich, Langmuir and Temkin isotherm models are all followed for the adsorption of Pb(II) on thiolated rice husk with high R^2 and low error function values[11,14].

Table 2: Adsorption isotherm error analysis for adsorption of Pb(II) ions on thiolated rice husk for different metal ions concentrations at 298 K and pH-5

Pb(II)	Freundlich	Langmuir	Temkin	D-R
$q_{e, exp}$	11.16 mg/g	11.16 mg/g	11.16 mg/g	11.16 mg/g
$q_{e, cal}$	11.86 mg/g	11.17 mg/g	11.45 mg/g	14.17 mg/g
SSE	1.0×10^{-3}	0.991	1.26×10^{-3}	11.45
SAE	0.1×10^{-2}	0.45	0.25×10^{-2}	8.47
ARE	1.55×10^{-2}	0.23	0.17×10^{-3}	4.41
HYBRID	2.47×10^{-3}	1.04×10^{-2}	0.47×10^{-3}	0.99
MPSD	3.45×10^{-5}	2.42×10^{-3}	0.15×10^{-5}	$0.74\ 10^{-2}$

Adsorption Kinetics

A study of the adsorption kinetics has been carried out using different kinetic models.

Generalised rate equation

$$r = k\,C^n \qquad (13)$$

Where r is the adsorption rate ($mgg^{-1}min^{-1}$), k is rate constant (min^{-1}), C is metal ion concentration (mg/L) and n is the order of reaction. A plot of log r vs. log C is a straight line and the values of k and n has been found to be $56.0 \times 10^{-2} min^{-1}$ and 0.98 respectively[6].

Lagergren first order rate equation

Lagergren first order equation represented by,

log (q_e–q) = log q_e - k_ad X t/ 2.303) (14)

where q_e and q (mg g^{-1}) are the amounts of Pb(II) adsorbed at equilibrium and at any time t (min) respectively, t (min) is the time of contact and k_{ad} is the adsorption rate constant (min^{-1}). A straight line plot for log(q_e - q) vs. t indicates the applicability this equation[6].

Pseudo second order rate equation

The data were further analyzed using pseudo second order rate equation.

$$t/q_t = 1/K_2 \; X \; 1/q_e{}^2 + t/q_e \qquad (15)$$

where K_2 is equilibrium rate constant for pseudo second order adsorption (gmg^{-1} min^{-1}), q_e and q_t (mg g^{-1}) is the amount of Pb(II) adsorbed at equilibrium and at any time and t (min) is the time of contact[6].

Values of pseudo first order and second order kinetics parameters are given in Table 3.

Intra-Particle Diffusion Study

The possibility of intra-particle diffusion has been explored by Morris Weber equation:

$$q = K_p \; x \; t^{1/2} \qquad (16)$$

where q is the amount of drug adsorbed per unit weight of adsorbent at various time intervals (mgg^{-1}), K_p is the intraparticle diffusion constant (mgg^{-1} min^{-1}) and t is contact time (min.). K_p as calculated from the slope of the linear plot of q vs $t^{1/2}$ and has been found to be 0.73 mgg^{-1}min^{-1}. A straight line plot that does not pass through the origin is obtained. The two distinct regions due to external mass transfer effect indicate that both surface adsorption and intraparticle diffusion contribute towards the rate determining step [11]. It can thus be inferred that the adsorption process follows pseudo first order kinetics and intraparticle diffusion contributes to the rate determining step[11].

Table 3: Adsorption kinetic parameters for adsorption of Pb(II) ions on thiolated rice husk for different contact time at metal ion concentration 300mg/L, 298 K and pH-5

Metal ion	**Pseudo-first order**			**Pseudo-second order**		
Pb(II)	**K_{ad} (min^{-1})**	**q_e (mg/g)**	**R^2**	**q_e (mg/g)**	**K_2 (gmg^{-1} min^{-1})**	**R^2**
	1.88×10^{-2}	8.91	0.988	14.0	1.52×10^{-3}	0.975

Effect of temperature and thermodynamic study

Experiments conducted at temperatures 298K, 303 K, 308K, 313K and 318K,for initial metal ion concentration 300mg/L, at pH 5 for a contact time of 150 minutes with an adsorbent dose of 250 mg with particle size 212 microns, show that the amount of Pb(II) adsorbed increases with increase in temperature, probably due to increase in number of sorption sites generated because of breaking of some internal bonds near the active surface sites of adsorbent[11]. The amount of Pb(II) adsorbed was found to be 11.16mg/g at 298K, 11.50mg/g at 303K, 11.78mg/g at 308K,11.99mg/g 313K and 12.16 mg/g at 318K.

Thermodynamic parameters for adsorption of Pb(II) on thiolated rice husk

The thermodynamic parameters can be determined using equations:

$$\ln K_c = \Delta S^o/R - \Delta H^o/RT \qquad (17)$$

$$\Delta G^o = -RT \ln K_c \qquad (18)$$

Where $K_C = C_{ad}/C_e$, is equilibrium constant and C_{ad} and C_e are the equilibrium concentrations (mg/L) of the metal ion on adsorbent and in the solution respectively[6]. The values of ΔH^0 and ΔS^0 have been computed from the slope and intercept of the plot of lnKc vs 1/T and found to be 22.1 KJ mol^{-1} and 90.9 KJ mol^{-1} respectively, which indicates the endothermic nature of adsorption process and increase in randomness at the adsorbent–adsorbate interface during the adsorption, while negative value of -5.25KJmol^{-1} of ΔG^0 confirms the feasibility and spontaneous nature of the adsorption process [11].

Column Adsorption Study

The effect of initial metal ion concentration as well as effect of flow rate has been studied for sequential bed as well as vertical columns[14,18] and results are discussed in this section.

Effect of metal ion concentration

The time for appearance of breakthrough and shape of breakthrough curve are very important characteristics for determining operation and the dynamic response of adsorption column, the breakthrough point was taken to be 0.5 C_t/C_o. Studies with metal ion inlet concentration 200mg/L, 250mg/L, and 300mg/L, show that the breakthrough occurred within a lesser period of time for higher inlet concentration. At lower inlet concentration, the breakthrough curve was flatter indicating a relatively wide mass transfer zone and film controlled process, as concentration increases the breakthrough curve became steeper and breakpoint time decreases as the binding sites become saturated more quickly [14]. Similar observations have been reported by Rao et al.[19] for adsorption of Cd(II) in a fixed bed mini column.

Effect of flow rate

For evaluating the performance of adsorption process for continuous treatment of wastewater on an industrial scale, flow rate plays an important role. Studies using thiolated rice husk in sequential bed and vertical bed columns with particle size 212 micron for influent concentration 200 mg/L, pH 5 and, flow rates 1.2 L/hr, 1.5 L/hr and 1.8 L/hr show that the breakthrough curve become steeper with a decrease in the breakthrough times and removal efficiency decreases with increase in flow rate (Fig. 2), the breakthrough point was taken to be 0.5 C_t/C_o. This can be explained by the fact that at lower flow rates, the residence time of the adsorbate in the column is greater and metal ions have more time to diffuse into the pores of adsorbent through intra particle diffusion, resulting in higher adsorption[18]. Similar dynamic flow characteristics of Pb(II) ions have been reported[20] in earlier studies.

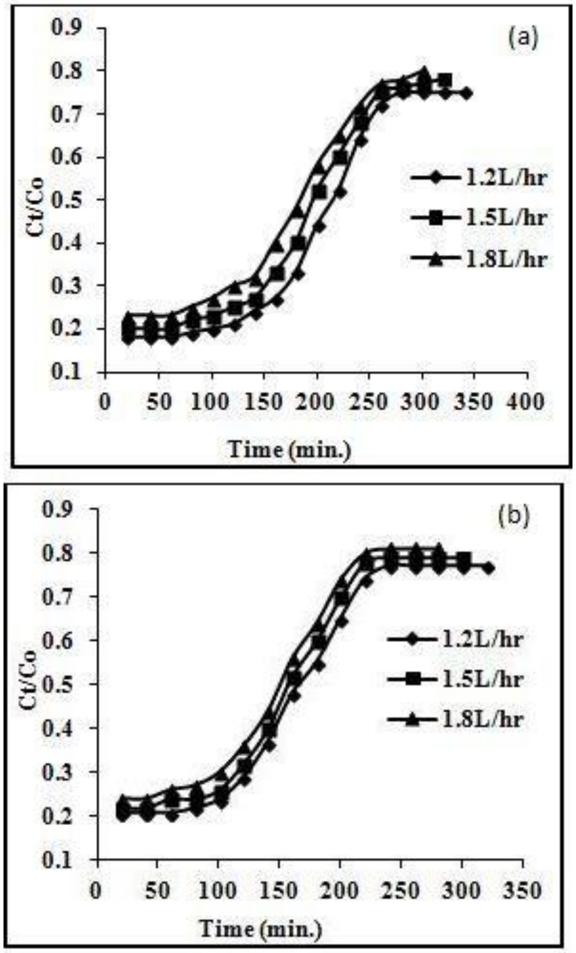

Figure 2: Breakthrough curves for adsorption of Pb(II) on thiolated rice husk at flow rates 1.2L/hr, 1.5 L/hr and 1.8 L/hr, influent metal ion concentration 200mg/L, pH 5 on particle size 212 micron in (a)sequential bed and (b) vertical bed column

Modeling of Breakthrough Curves

Adsorption kinetics and column performance can be well described using Thomas and Yoon–Nelson models.

(a) Thomas model

Thomas model is based on the assumption that the process follows Langmuir kinetics of adsorption–desorption with no axial dispersion.The expression developed calculates the maximum solid phase concentration of the solute on the sorbent and the adsorption rate constant for a continuous adsorption process in column. The linear form of the model is given as:

$$\ln\left[\frac{C_o}{C_e}-1\right]=k_{TH}q_o\frac{M}{Q}-k_{TH}\,C_o\,t \qquad (19)$$

Where K_{TH} is Thomas rate constant (l $min^{-1}mg^{-1}$); q the maximum solid - phase concentration of the solute (mg g^{-1}), M is the mass of adsorbent (g); Q the flow rate (l min^{-1}). The kinetic coefficient K_{TH} and the adsorption capacity of the bed q_o can be determined from plot of $[\ln(C_o/C_t)-1]$ against time at a given flow rate[14,18]. The values of K_{TH} are found to be 7.8×10^{-5} for sequential bed column and 7.5×10^{-5} for vertical column. The values of q_o are found to be 873.0 for sequential bed column and 762.7 for vertical column.

(b) The Yoon–Nelson model

This model was derived based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent[11,13]. The linearized model for a single component system is expressed as:

$$\ln\frac{C_t}{C_o}-C_t = K_{YN}t - \tau K_{YN} \qquad (20)$$

where K_{YN} is the rate constant (L mg^{-1}); the time required for 50% adsorbate breakthrough (min); τ is the breakthrough time (min). The kinetic coefficient K_{YN} and τ can be determined from A plot of $[\ln(C_t/C_o)-C_t]$ against time t is a straight line with slope K_{YN} and intercept τ [14,18]. The values of K_{YN} is found to be 0.016, for the sequential bed column and 0.014 for vertical column. The values of τ are 219.3 for sequential bed column and 186.0 for vertical column.

Desorption Study

Adsorption of Pb(II) on any adsorbent can be by physical, chemical bonding, ion-exchange or combination of all [21]. Attempts were made to desorb Pb(II) ions from thiolated rice husk using 0.5M solutions of HCl at flow rate 1.2 L/hr.

The desorption efficiency can be calculated from the equation:

$$\text{Desorption Efficiency} = \frac{M_d}{M_{ad}} \times 100$$

Where M_{ad} is metal adsorbed (mg/g) and M_d is metal desorbed (mg/g).

It was observed that the desorption of Pb(II) with acidic solution was very high, desorption of Pb(II) from thiolated rice husk was found to be 75% .The higher percentage of desorption indicated that ion exchange mechanism may also play a significant role in the sorption process.

Effect of mutual interference of metal ions on adsorption of Pb(II)

Experiments were performed to investigate the influence of Pb(II) on the uptake of Pb(II) from binary solutions by varying the concentration ratios of Pb(II) + Ni(II) in the range 1:0, 1:1, 1:2, 1:3 and 1:4 for fixed Pb(II) ion concentration of 30mg/L, 60mg/L and 90mg/L. Percentage removal of Pb(II) ions decreases from 93.3 to 43.0%, 89.2 to 27.0% and 82.0 to 18.0% for increasing Ni(II) content at Pb(II) ions concentration of 30 mg/L, 60 mg/L and 90 mg/L respectively (Fig. 3).

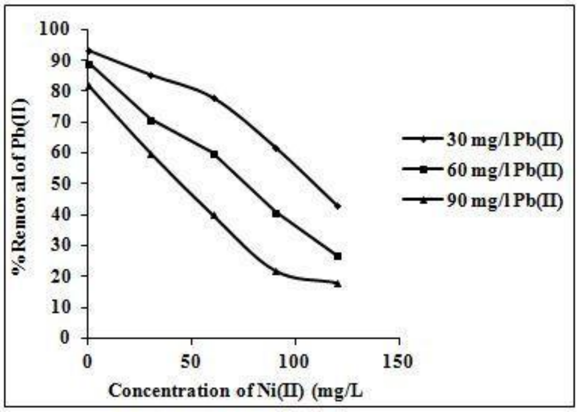

Figure 3: Percentage removal of Pb(II) from [Pb(II) +Ni(II)] mixture for various Pb(II) ion concentrations on thiolated rice husk at 298 K, pH 5 on particle size 212 micron

The equilibrium data obtained from binary adsorption system have been analysed using q'_e/q_e ratios, where q_e is amount adsorbed for single component system at equilibrium and q'_e denotes the equilibrium amount adsorbed in the presence of other component[11].

In general, three possible types of behaviour are exhibited: $q'_e/q_e > 1$ indicates Synergism (the effect of presence of the second component favours the adsorption of the primary adsorbate and adsorption from mixture is greater than that from the individual adsorbate solution), $q'_e/q_e < 1$ shows antagonism (the effect of the second component hinders the adsorption of the primary adsorbate and adsorption from mixture is less than that of the individual adsorbate in single component solution), $q'_e/q_e = 1$, non- interaction i.e there is no effect on the adsorption of the adsorbate in the presence of the other component in the mixture. The q'_e/q_e ratios are found to be 0.28 thiolated rice husk, which indicates that the adsorption of the Pb(II) was suppressed by the presence of Ni(II) ions in the binary solution, hence the effect of the mixtures is antagonistic that is there is an inhibitory effect of one metal on binding of the other metal[22].

The Langmuir competitive model (LCM)

To further analyse the nature of competition among Pb-Ni ions, the Langmuir competitive model has been applied to the binary sorption equilibrium data using Eq.(14)

$$(C_{e1}/C_{e2}\ X\ q_{e1}) = (C_{e1}/q_{m1}\ X\ C_{e2}) + (K_{L2}/K_{L1}\ X\ q_{m1}) \tag{19}$$

Where q_{m1} (q'_e), K_{L1} and K_{L2} are physical parameters, C_{e1} and C_{e2} are equilibrium concentrations of Pb(II) and Ni(II) in the mixtures of solutes. Values of K_{L1}(K_{L2}/K_{L1}) and q_{m1}(q'_e) of Langmuir competitive model were found to be 3.25×10^{-2} and 3.08 respectively. The value of $q_{m1}(q'_e) < 1$, indicates that the adsorption of Pb(II) was depressed by presence of Ni(II) ions in the binary solution[23,24].

Conclusion

Results suggest that thiolated rice husk can be effectively used as adsorbent for removal of Pb(II) ions from aqueous medium. Continuous column studies suggest that the bed capacity for sequential bed column is greater than that has been obtained for vertical bed column. It is also found that sequential bed is easier to handle and use, there is no possibility of clogging and is slightly better than that of vertical column and can be considered for use in small scale industries. The study of binary mixture of Pb(II)+Ni(II) shows that the adsorption of Pb(II) was suppressed by the presence of Ni(II) ions in the binary solution and the effect of the mixtures is antagonistic in nature.

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