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Removal of Lead from Aqueous Medium Using Xanthate Modified Apple Juice Residue

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Abstract

This study investigated the feasibility of chemically modified apple juice residue as a novel type of adsorbent for lead removal from aqueous medium. FTIR studies were carried out to understand the type of functional groups in unmodified and modified apple juice residue responsible for metal binding process. Equilibrium adsorption data were fitted in terms of monolayer adsorption at pH 4 by batch method. The kinetics was studied for biosorption processes and data were described by pseudo second order model. The equilibrium constant and Gibbs free energy of the adsorption at 25 ºC were determined. The mechanism of sorption was found to obey the ion exchange and complexation method.

Keywords: *Heavy metal, biosorption, xanthate, ion exchange, complexation*

Introduction

The presence of heavy metals in the environment has become a great concern due to their increasing discharge, toxic nature and other adverse effects into the receiving water bodies and thereby affecting significantly the quality of water supply. Metals are considered as toxic pollutants and non biodegradable in nature which undergo transformations and have great environmental, public health and economic impacts.[1] Lead is one of the toxic environmental pollutants which is found in nature and also found as introduced contaminant into the environment. Its presence even at trace levels can pose health hazards[2]. Acute lead poisoning usually affects gastrointestinal tract, nervous system, liver and kidney, reproductive system, brain, and sometimes even causes death. Chronic exposure to lead is associated with sterility, abortion, stillbirths, and neonatal deaths.[3,4] Many physicochemical methods including sorption to metal oxide, clay, activated carbon, organic sorbents have been extensively used to remove toxic metals, in recent years an alternative technology called bio-sorption by the usage of biomass, fiber, peat, living plants and bacteria as adsorbents is in progress. Biosorbents are cheap materials often with high affinity and binding capacity for metals and are readily available in most places.

Among the adsorbents used to remove heavy metals, those containing sulfur-bearing groups have a high affinity for heavy metals but a low affinity for light metals. From the

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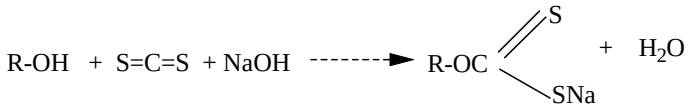
different sulphur bearing compounds, xanthates are found most prominent because they are easy to prepare with relatively inexpensive reagents, highly insoluble and have high stability constant values of the metal complexes formed according to HSAB classification system. Xanthates are formed by reacting on organic hydroxyl-containing substrate with carbon disulfide under caustic condition.[5,6] The basic chemical reaction is shown below.[7]



Apple juice residue is mostly composed of cellulose, hemicellulose, pectin, lignin, chlorophyll pigments and other low molecular weight hydro-carbons.[8] Many of these contain several hydroxyl functional groups, which make the apple juice residue a potential substrate for the synthesis of xanthates. In the present work, we attempted to prepare novel xanthated material for adsorption of lead. The fractional attainment to the equilibrium, the mechanism of sorption, the equilibrium rate constant, the order of the reaction and hence the standard Gibbs-free energy for the reaction at 25 ºC were established.

Experimental Methods

Apple juice residue obtained from local market was first washed thoroughly with distilled water to remove soluble material and dried in an oven at 50°C for 50 h. The dried apple residue was crushed and sieved into different fractions. Approximately 40 gm of apple residue was treated with 250 ml of 17% NaOH solution for 2 h to remove chlorophyll pigment and low molecular weight compounds. Then 10 ml of CS_2 was added and mixture was stirred in rotary shaker for 24 h. The obtained products were washed several times with distilled water. After drying in an oven at 30°C overnight, the dried solid was stored in desiccators at room temperature. The prepared xanthate adsorbent was abbreviated as MAJR (modified apple juice residue) hereafter for convenience.

To determine the maximum amount of active sites on modified adsorbent, 30 mg of dried H^+-form gel and 30 mL of 0.01M of NaOH solution were equilibrated for 24 h.[9] Finally the acid-base titration was employed for supernatant solution[10]. Fourier transform infrared (FTIR) analysis was performed to identify functional groups on apple juice residue (AJR) and chemically modified apple juice residue (MAJR). FTIR spectra were obtained using a spectroscope (JASCO FT/IR, Japan) at resolution 1 cm^{-1}. Pressed potassium bromide (KBr) pellets at a sample/KBr weight ratio of 1:100 were scanned and recorded between 4000 and 400 cm^{-1}.

The adsorption of Pb^{+2} was investigated in batch equilibrium experiments. The experiments were carried out in 125 mL conical flasks containing 20 mL of metal ion solutions of different concentrations and 20 mg of the adsorbents, shaken for 24 h at 100 rpm in a mechanical shaker. A series of adsorption experiments were conducted at different initial pH to study adsorption mechanism. After the desired shaking period for each batch, the concentration of Pb^{2+} ion was measured using atomic absorption spectrophotometer (AAS; Perkin Elmer AA-100).

The amount of metal adsorbed was calculated using the following equation:

$$q = (C_i - C)\ V/m \qquad (1)$$

where, C_i-initial concentration of metal ion mmol/L; C –Concentration of metal ion after certain period of time mmol/L; m –mass of adsorbent g; V- the volume of the solutions mL.

Results and discussion

Characterization of adsorbent

The broad and intense absorption peaks at around 3403 cm^{-1} from FTIR spectrum shown in Fig. 1, corresponds to the O-H stretching vibration due to inter and intra-molecular hydrogen bonding of polymeric compounds such as phenols, alcohols, and carboxylic acids, as in cellulose, pectin and lignin, thus showing the presence of free hydroxyl groups on the adsorbent surface. Similarly, peak at 2930 cm^{-1} corresponding to C-H stretching, 1749 cm^{-1} to stretching vibration of bond due to non ionic carboxylic groups: –COOH and $–COOCH_3$. The peaks at 1652 and 1448 cm^{-1} are due to asymmetric and symmetric stretching vibration of C=O in ionic carboxylic groups (-COO-), respectively. Aliphatic acid group vibration at 1259 cm^{-1} may be assigned to deformation vibration of C = O and stretching formation of –OH of carboxylic acids and phenols.[11] Peaks at 1078 cm^{-1} may be due to stretching vibration of C–OH of alcoholic groups and carboxylic acids.[5]Due to the chemical modification some distinct changes are noted in the spectrum of MAJR. The broad peak at 3403 cm^{-1} in the AJR shifts to 3398 cm^{-1} in the MAJR which indicates that the hydroxyl groups have combined with CS_2. The major adsorption characteristic bands of xanthate groups lie in the region 800-1225 cm^{-1}. The presence of sulfur groups in the MAJR has been identified by the appearance of new peaks at 538, 1050 and 1165 cm^{-1} corresponding to C–S, C= S and S–C–S symmetric stretching.[12]

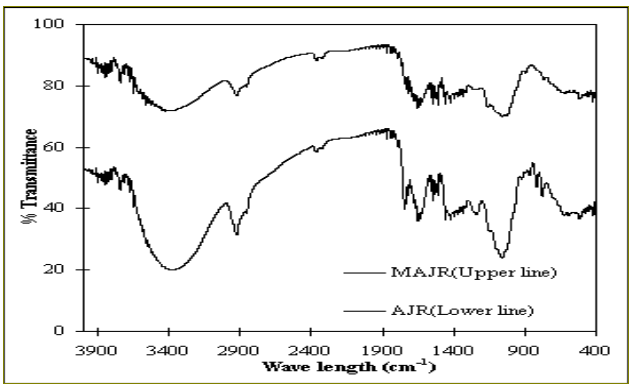


***Figure 1**: FTIR analysis result on the surface of AJR and MAJR*

The maximum amount of active sites on modified sample was found as 2.52 mol/kg. It revealed that the prepared adsorbent would possess higher amount of ion exchangeable sites for metal cation.

Adso*rption equilibrium*

To investigate the optimal pH for maximum adsorption of Pb^{+2} ions the experiment was examined over a pH range 3.5 to 4.5 by using initial Pb^{+2} concentration of 0.024 mmol/L to 2.41 mmol/L. The effect of initial concentration on efficiency of MAJR to remove Pb^{+2} at different pH is depicted in Fig. 2. The maximum adsorption of Pb^{+2} was obtained at pH 4.

The effect of pH can be explained considering the surface charge on the adsorbent material. At low pH, adsorption of Pb^{2+} ions was intensively decreased towards a fixed number of adsorption sites due to high positive charge density of protons on the surface sites. This is a result of competition between Pb^{2+} ions and H_3O^+ for binding sites.[13] With increasing pH, electrostatic repulsion decreases due to reduction of positive charge density on the sorption sites thus resulting in an enhancement of metal adsorption to get optimum value. Above this, the adsorption of Pb^{2+} was decreased with increasing pH, owing to the interaction between OH^- and Pb^{2+} ions followed by solvation and hydrolysis in the solution. The process involved is as follows.[7]

$$Pb^{+2} + nH_2O \dashrightarrow Pb(H_2O)_n^{2+}$$

$$Pb(H_2O)_n^{2+} \dashrightarrow Pb(H_2O)^{n-1} + H^+$$

$$nPb^{2+} + mH_2O \dashrightarrow Pb(OH)_m^{2n-m} + mH^+$$

The pH speciation shows that the dominant species is $Pb(OH)_2$ at PH >5 and Pb^{2+} and $Pb(OH)^+$ at pH < 5. If pH of the media controlled carefully during experiment, the adsorption characteristics of Pb^{2+}onto MAJR were investigated by fitting data obtained for the degree of surface coverage into different adsorption isotherms which corresponds to the relationship between the mass of the solute adsorbed per unit mass of the adsorbent q_e and the solute concentration for the solution at equilibrium C_e.

The sorption data was tested against Langmuir and Freundlich adsorption isotherm models. The linear form of the Langmuir model as shown below was used[14].

$$C_e/q_e = 1/bq_m + C_e/q_m \qquad (2)$$

Linear plots of C_e/q_e vs C_e(Fig. 3) were employed to determine the value of q_{max} (mmol/g) and b(L/mmol) and are the ultimate adsorption capacity and relative energy(binding constant) of adsorption respectively. Linearity of the plots indicated the applicability of the adsorption isotherm. The parameters of the Langmuir isotherm for each heavy metal estimated from Fig. 2 at pH 3.5, 4 and 4.5 are shown in Table 1 by assuming that only monolayer adsorption took place by MAJR and the maximum Pb^{+2} uptake values obtained was 1.22 mmol/g at pH 4.

The essential characteristics and the feasibility of the Langmuir isotherm in terms of a dimensionless constant, separation factor or equilibrium parameter R_L, which is defined as[11].

$$R_L = 1/ (1 + bC_i) \qquad (3)$$

The R_L value indicates the shape of the isotherm as $R_L > 1$: unfavourable, $R_L = 1$: linear , $0 < R_L > 1$: favourable, $R_L = 0$: irreversible adsorption.

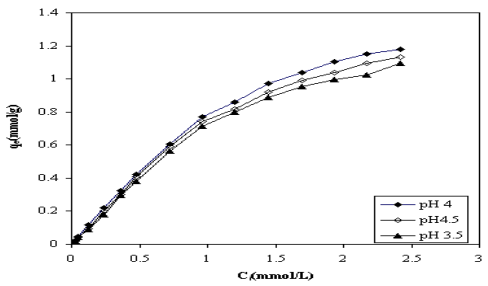


***Figure 2**: Effect of initial concentration for adsorption of Pb^{2+} at different pH values*

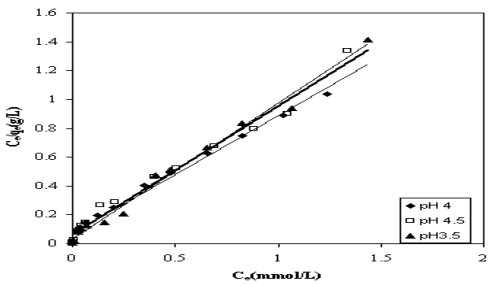


***Figure 3**: Langmuir adsorption isotherms for Pb^{2+} adsorption at different pH values*

The adsorption data obtained were then fitted to the Freundlich adsorption isotherm which is the earliest relationship known describing the adsorption equilibrium and is expressed by the following equation[15].

$$\log q_e = \log K + 1/n \log C_e \quad (4)$$

The Freundlich isotherm constants K and n are constants incorporating all factors affecting the adsorption process such as of adsorption capacity and intensity of adsorption. The constants K and n were calculated from equation 4 and Freundlich plots as shown in Fig. 4 are depicted in Table 1. The values of n between 1 and 10 (i.e. 1/n less than 1) represent a favorable adsorption [16]. The n values obtained for adsorbent considered for study represent a beneficial adsorption

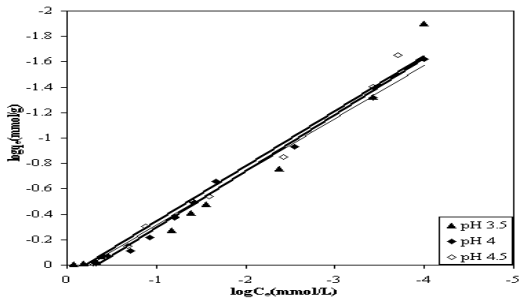


***Figure 4**: Freundlich plot for the adsorption of Pb^{+2} at different pH values*

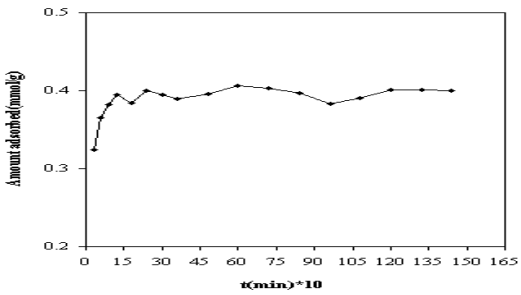


***Figure 5**: Effect of contact time for adsorption of Pb^{+2} by MAJR*

From the Table 2 the data obtained represent a favorable adsorption for the concentration range studied. The equilibrium constant of adsorption of Pb^{2+} onto MAJR is related to the free energy of adsorption as follows[17]:

$$\Delta G = -RT \ln K \quad (5)$$

where ΔG is the Gibbs free energy change (KJ/mol), R is the ideal gas constant (8.314/mol k), T is the solution temperature (Kelvin), and K is the thermodynamic equilibrium. The values of ΔG for adsorption of Pb^{+2} at pH 3.5, 4 and 4.5 were 33.20, 35.31 and 33.53 KJ/mol, respectively. The negative value for Gibbs free energy shows that the adsorption process of Pb^{2+} on alkali-treated apple juice residue is spontaneous in nature.

***Table 1**: Adjustable parameters for the isotherms models for Pb^{+2} adsorption by MAJR at different pH values*

Langmuir constants				Freundlich constants			Gibb's free energy change ΔG(kJ/mol)
pH	q_{max} (mmol/g)	B (L/mmol)	Correlation coefficient	K(mmol/g)	n	Correlation coefficient	
pH 3.5	1.06	11.91	0.9903	1.39	2.2	0.9366	33.20
pH 4.0	1.22	27.91	0.9987	1.26	2.4	0.9881	35.31
pH 4.5	1.12	13.61	0.9912	1.22	2.3	0.9811	33.53

***Table 2**: Separation factor or equilibrium parameter R_L for adsorption of Pb(II) at pH 4.*

Initial concentration Ci(5mmol/L)Pb(II)	Initial concentration Ci(200mmol/L)Pb(II)	Initial concentration C_i(500mmol/L)Pb(II)
0.598	0.036	0.014

The study of adsorption dynamics describes the solute uptake rate and evidently these rate controls the residence time of adsorbate uptake at the solid–solution interface so essential for a successful application of the adsorption process in wastewater treatment. It was observed from Fig. 3 that the amount of Pb^{2+} adsorption increased with contact time and occurred in two stages i.e. initial rapid uptake within 15-20 min followed by subsequent slow uptake, until steady state condition was attained.

The rate kinetics of Pb^{2+} adsorption onto MAJR was analyzed by using Lagergren and pseudo-second order model. The conformity between experimental data and the model predicted values was expressed by correlation coefficient.

The intergral form of Lagergren (pseudo first order) model generally expressed as follows[8].

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \quad (6)$$

The kinetics of adsorption process may also be described using pseudo-second-order rate equation. This assumes that the rate is proportional to the square of the number of remaining free surface sites. The linearized form of equation is expressed as[13];

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (7)$$

The applicability of the Lagergren and pseudo-second order models were examined by each linear plot of log $(q_e - q_t)$ vs. t, (t/q_t) vs. t, respectively and are presented in Figs 6 and 7, respectively. The values of rate constants and correlation coefficients for each model are shown in Table 3. Obviously, the adsorption process could be well described by the pseudo-second order equation, indicating the process mechanism to be chemical adsorption being the rate controlling step with the formation of monolayer coverage on the adsorbent surface.[13]

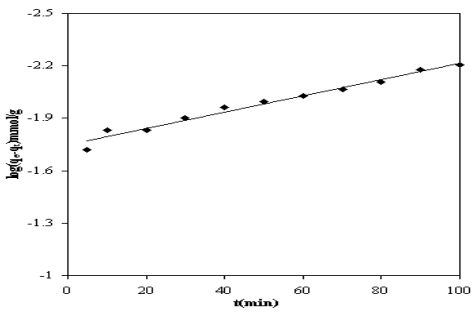


***Figure 6**: Lagergren plot for adsorption of Pb^{+2} by MAJR*

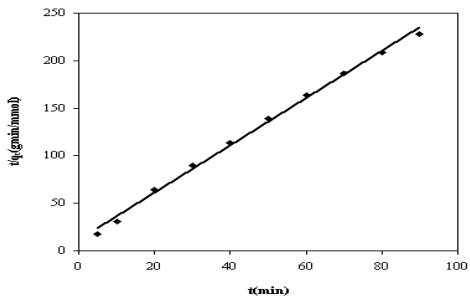


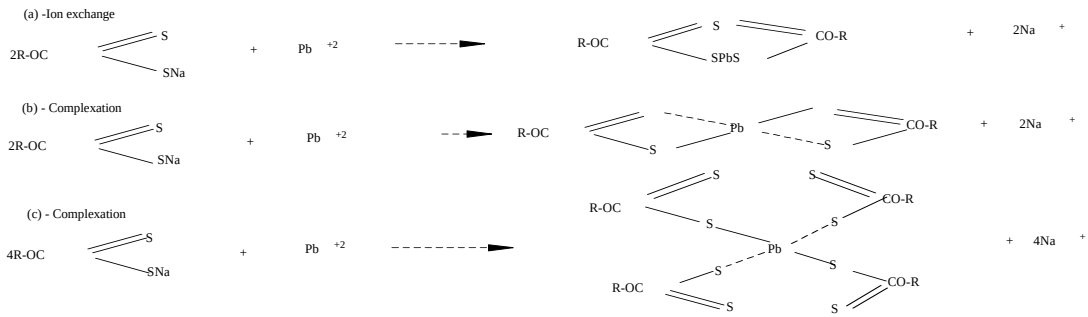
***Figure 7**: Pseudo-second order plot for adsorption of Pb^{+2} by MAJR*

***Table 3**: Rate kinetics for adsorption of Pb^{2+} with comparison of calculated and experimental q_e values.*

q_e expt mmol/g	Lagergren			Pseudo second-order		
	k_1 1/min	q_e cal, mmol/g	Correlation coefficient(R^2)	k_2 g/mmol.min	q_e mmol/g	Correlation coefficient(R^2)
0.420	0.010	0.011	0.976	0.556	0.402	0.999

Mechanism of adsorption

The identification of xanthate functional groups from FTIR on the surface MAJR provides the better understanding of adsorption mechanism. From the affirmation between maximum amount of exchanged protons on adsorbent and amount of metal uptake, the adsorption of Pb^{2+} ion on the surface may be regarded as ion- exchange as well as some complexation and or chelation. By ion exchange, two negative charged sulfur atoms of MAJR participate in capturing one divalent metal ion. However, complex formation occurs between four sulfur atoms and one divalent metal ion (Scheme 1). It is postulated that metal ion adsorption process could undergo both ion exchange and complex formation.[8,13] Because lead belong to transition metals, which have empty orbitals that can be occupied by electrons to form complex and considering steric hindrance, mechanism (b) is the most possible adsorption process.[7,18]



***Scheme 1**: Plausible adsorption mechanisms for adsorption of Pb^{+2} ions onto MAJR*

In addition, during the adsorption process equilibrium pH values were increased if no buffer solution was added into the experimental solutions. This phenomenon can be explained by proposing that Na^+ ions were released into the solutions according to both ion exchange and complexation mechanisms they then combined with OH^- ions to form alkali which strengthened the alkalinity of the solutions.

Conclusions

This work indicated that adsorbent devised by incorporation of xanthate group onto the surface of apple juice residue could be used as viable bio-sorbent for the treatment of Pb^{2+}ions bearing wastewater streams. The maximum amount of exchangeable sites possessing in novel adsorbent is 2.52 mol/kg. The maximum amount of Pb^{2+} ions uptakes was found 1.22 mmol per unit gm of adsorbent at pH 4. The adsorption data pertaining for adsorption process is thermodynamically feasible and good agreement with Langmuir isotherm and pseudo second-order kinetic model. During the adsorption, predominant ion-exchange mechanism is supposed to be involving between metal ion and cation containing with sulphur at xanthate group and proved by FTIR spectrum. The quantity of exchanged proton was highly relative to the concentration of metal adsorbed. From the superior result on Pb^{2+}, it might be helpful for removing other toxic heavy metals like cadmium, zinc, cupper, nickel and mercury containing wastewater.

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