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Low-Cost Adsorption Studies Solutions Using Lemon Peel

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ABSTRACT
Due to their acute and long-term exposure through the air, water, and food chain, heavy metals play a role in a number of harmful environmental health impacts. Traditional methods of metal removal are frequently constrained by their expense and inefficiency at low concentrations. Adsorption, or the utilisation of inactive biomass as adsorbents, presents a compelling possible substitute for their current practises. Lemon peel and the vast biomass found in plantago aquatica are naturally occurring and can be used to remove metal at a reasonable cost. The batch investigations showed that the biomass dose, solution pH, and beginning metal concentration all had an impact on the adsorption. As metal concentration rose, the percentage of metal removal fell. The equilibrium data were analysed using three adsorption isotherm models: Langmuir, Freundlich, and Dubinin-Radushkevich. The Langmuir isotherm model (R21) best describes equilibrium. The thermodynamic characteristics of the process have been determined using isotherm investigations. Adsorption kinetic characteristics such the intraparticle diffusion rate constant, pseudo-first order, and second order were identified and fitted with the second order kinetic model. For Cd (II), Pb (II), Zn (II), and Cu, the highest amount of heavy metals (qmax) adsorbed at equilibrium was 17.3, 31.05, 25.25, 16.4, and 24.8 mg/g mango peel.

Keywords - Adsorption, heavy metals, equilibrium, thermodynamics, kinetics, packed bed column

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I. INTRODUCTION

The majority of adsorption research has been concentrated on inexpensive adsorbents. Utilizing plant wastes for waste water treatment has a number of benefits, including the use of straightforward procedures, minimal processing requirements, good adsorption capacity, selective heavy metal ion adsorption, cheap cost, and free availability. In this project, lemon peel is used for batch studies.

The adsorbent lemon peel was used in the trials. To get rid of dirt and other impurities, the adsorbent samples were taken from a neighbouring region and cleaned many times with distilled water. After drying, it was ground with a household mixer and sieved to a size of 250 mesh. The sample is cleaned with distilled water to remove the colour before being dried for 24 hours at 80 degrees Celsius. The dried material was not subjected to any chemical or physical processing before being placed in sealed vials for future usage.

The analytical grade reagents utilised in this study were all purchased from Merck Germany. Metal nitrate salts in double-distilled water were used to generate stock solutions of cadmium, lead, zinc, chromium, and copper. The stock solutions were then diluted to the necessary concentrations. Metal ions in water samples obtained using the ASTM techniques Cd(D3557), Pb(D3559), Zn(D1691), Cr(D1687), and Cu can be determined using test methods.(D1688).

Fig 1. Fine grains of dry lemon peel

II. MATERIALS AND METHODS

2.1. Adsorbent:

The adsorbent lemon peel was used in the trials. To get rid of dirt and other impurities, the adsorbent samples were taken from a neighbouring region and cleaned many times with distilled water. After drying, it was ground with a household mixer and sieved to a size of 250 mesh. The sample is cleaned with distilled water to remove the colour before being dried for 24 hours at 80 degrees Celsius. The dried material was not subjected to any chemical or physical processing before being placed in sealed vials for future usage.

2.2. Reagents

The analytical grade reagents utilised in this study were all purchased from Merck Germany. Metal nitrate salts in double-distilled water were used to generate stock solutions of cadmium, lead, zinc, chromium, and copper. The stock solutions were then diluted to the necessary concentrations. Metal ions in water samples obtained using the ASTM techniques Cd(D3557), Pb(D3559), Zn(D1691), Cr(D1687), and Cu can be determined using test methods.(D1688).

2.3. Instrument

Atomic absorption spectrophotometer (Thermofisher iCE:3000) measurements of the initial metal concentration and the concentration of the metal still present in the solution were made.Utilizing a PERKIN ELMER model Spectrum Two, FTIR spectra were collected. The dried adsorbent sample's outer surface micro porosity and pore size were investigated using a SEM. (HITACHI SU 6600).

Fig 2. Photograph of Atomic absorption spectrophotometer

2.4. Batch studies

Using a temperature-controlled incubator shaker set at 25°C, a volumetric flask was filled with a preset quantity of dry adsorbent (0.1g) and 100ml of a metal solution. The used metal ion concentrations ranged from 10 to 100 mg/l. For batch experiments, a contact period of 120 minutes was utilised and the pH of the solution was kept at 5.50.5. The pH of the metal solution was changed to various values between 2 and 7 in order to explore the impact of pH. With the help of 0.1 N HCl and 0.1 N NaOH solutions, the desired pH was changed. The samples were then filtered to remove any tiny particles before being examined with an atomic absorption spectrophotometer to determine the presence of metal ions.

2.5. Equilibrium studies

To ascertain the type of adsorption isotherms and the adsorption capacity of the adsorbent for the removal of metal ions, adsorption equilibrium studies were carried out. Using 1g/l (dry weight) adsorbent, the initial metal concentrations were changed for the isotherm investigations from 10 to 100 mg/l. The adsorption flasks were shaken at 200 rpm in an incubator while samples were taken at predetermined intervals, the residual metal concentration was determined, and the biomass was then separated by filtration.

2.6. Kinetic Studies

In a volumetric flask, kinetic experiments were conducted, and samples were taken at intervals ranging from 5 to 120 minutes. The samples' residual metal content was examined.

III. RESULTS AND DISCUSSION

To ascertain the influence of the operating parameters on metal ion adsorption, extensive research was conducted. The operational parameters investigated included the equilibration period, biomass dose, and solution pH. The absorption of metal ions by mango peel biomass was first assessed under batch conditions.

- Effect of contact time
- Effect of Adsorbent dose
- Effect of varying concentration of metal ions
- Effect of pH
- Adsorption isotherms

3.1. Effect of contact time

The amount of metal ions adsorbed at equilibrium time represents the adsorbent's maximum capacity for adsorption under these specific circumstances. The outcome shown that metal ion adsorption increased over time up to 1 hour before becoming practically constant at the conclusion of the experiment. Conclusion: The rate of metal binding with biomass is higher during the initial stages, progressively declines, and nearly stays constant after 120 minutes. As soon as the adsorbent is added to the system, its active adsorption sites begin to participate in metal complexation.

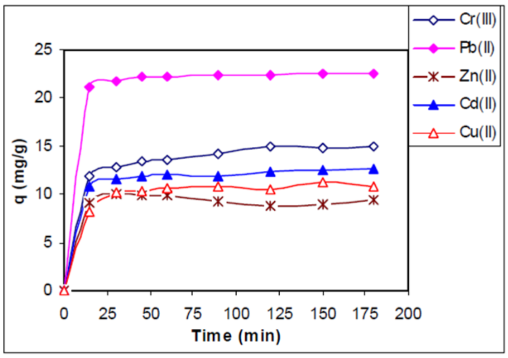

Fig 3. Metal uptake rates over a range of time periods (initial concentration = 50 ppm, adsorbent dosage = 0.3 g/100 ml metal solution, temperature = 25–2 oC, pH = 5, orbital shaking speed = 200 rpm, time = 180 min.)

3.2. Effect of Adsorbent dose

Figure 4. illustrates how biomass dose affects metal adsorption. With increasing adsorbent dosage, metal ion adsorption increased until equilibrium was obtained at adsorbent dosages greater than 0.4gm/100ml. With increasing biomass, more metal was removed on a percentage basis.

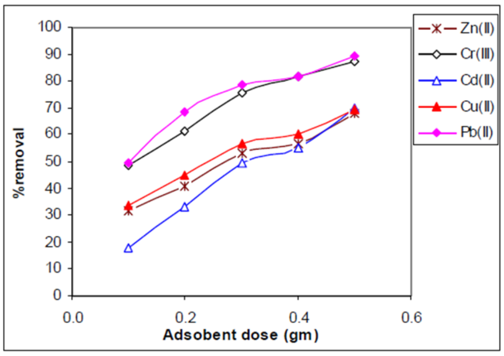

Fig 4. Effect of adsorbent dose on metal adsorption (initial concentration = 50 ppm, adsorbent dose = 0.1 to 0.5 g/100 ml metal solution, temperature = 25 2 oC, pH = 5, orbital shaking speed = 200 rpm, time = 120 min.)

3.3. Effect of varying concentration of metal ions

Higher metal ion concentrations resulted in lower % removal because there were fewer accessible adsorption sites due to adsorption site saturation. The ratio of the initial number of moles of metal ions to the available adsorption sites was larger at higher metal ion concentrations, which led to a lower adsorption percentage.

Contrary to the percentage uptake, the amount of metal ions adsorbed at equilibrium rose as the initial metal ions concentration increased from 10 mg/L to 100 mg/L. This happened as a result of the concentration gradient's increased driving force, which overcame all metal ion mass transfer resistance between the aqueous and solid phases and accelerated the likelihood of a collision between metal ions and sorbents, leading to a greater uptake of metal ions.

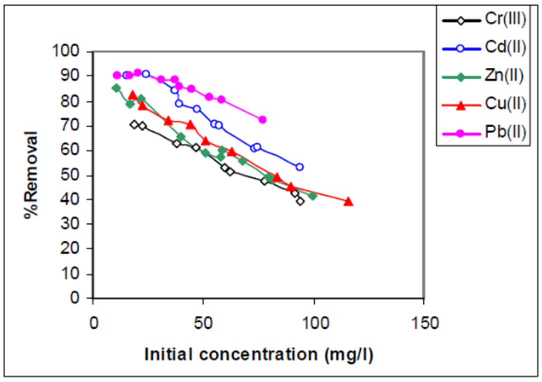

Fig 5. Effect of increasing metal ion concentration (Initial concentration: 10 to 100 ppm; Adsorbent dose: 0.3 g/100 ml metal solution; temperature: 25–2 oC; pH: 5; Orbital shaking speed: 200 rpm; Time: 120 min.)

3.4. Effect of pH

In the pH range of 2 to 8, the impact of solution pH on the adsorption of metal ions onto mango peel was assessed. At pH6, Pb(II), Cu(II), and Zn(II) had the highest removal efficiencies for Cd(II) and Cr(III) adsorption with mango peel. Mango peel absorbed the fewest metal ions at pH 2, which had the maximum acidity. Between 80% and 95% of the material was removed in the pH range of 3 to 7, and this clearance rate rose quickly. The adsorption effectiveness was discovered to decline at decreasing pH values.

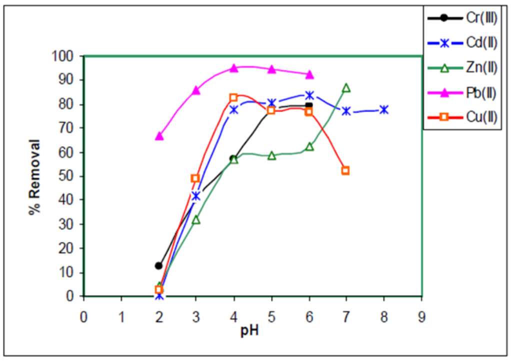

Fig 6. Effect of pH variation on the adsorption of metal ions (pH range: 2 to 8; initial concentration: 50 ppm; adsorbent dose: 0.3 g/100 ml metal solution; temperature range: 25 to 22 oC; orbital shaking speed: 200 rpm; time interval: 120 min.)

3.5. Adsorption isotherms

Certain constants that indicate the surface characteristics and affinity of the sorbent are used to describe an adsorption isotherm. The Freundlich constants k and 1/n, which were calculated for the adsorption capacities and intensities of Cd(II), Pb(II), Zn(II), Cr(III), and Cu(II) at various temperatures, are listed in Table 4.1.The Cf/q vs Cf plot was used to establish the Langmuir constants for qmax and b. The Langmuir isotherms' applicability suggests that monolayer adsorption exists in the experimental setting. The chemical or physical characteristics of the adsorption process are not explain The aforementioned information indicates that the affinity order of mango peel is Pb>Cr>Zn>Cd>Cu. The Langmuir isotherm shows that a metal ion monolayer forms on the adsorbent. From the plot of log q vs log Cf, linear regression was used to calculate the constants K and 1/n. K represents the strength or degree of adsorption. The Langmuir isotherm constants.

While 1/n is used to determine if adsorption reduces with rising metal ion concentrations (at 1/n=1) or remains constant (at 1/n=1). The experimentally determined qmax for Pb, Cr, Zn, Cd, and Cu ions in mango peel is found to be 31, 24.8, 24.5, 16.7, and 16 mg/g for all five, which is comparable to the qmax derived theoretically.

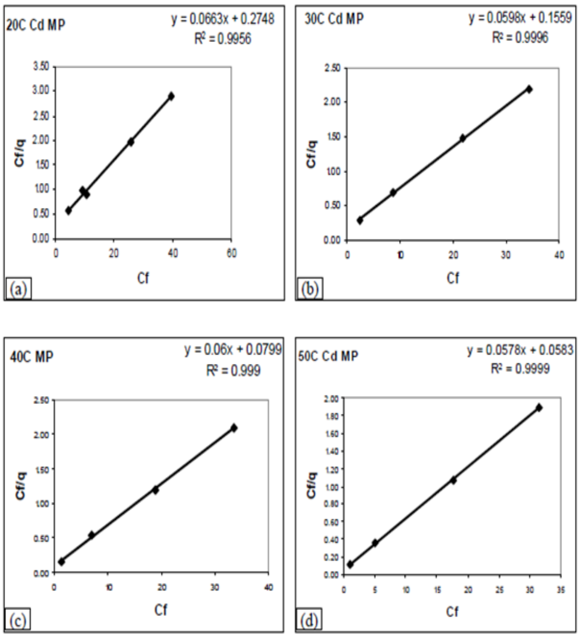

Fig 7. (a), (b), (c), (d) Langmuir plot for cadmium adsorption at 20,30, 40 and 50^{oC}

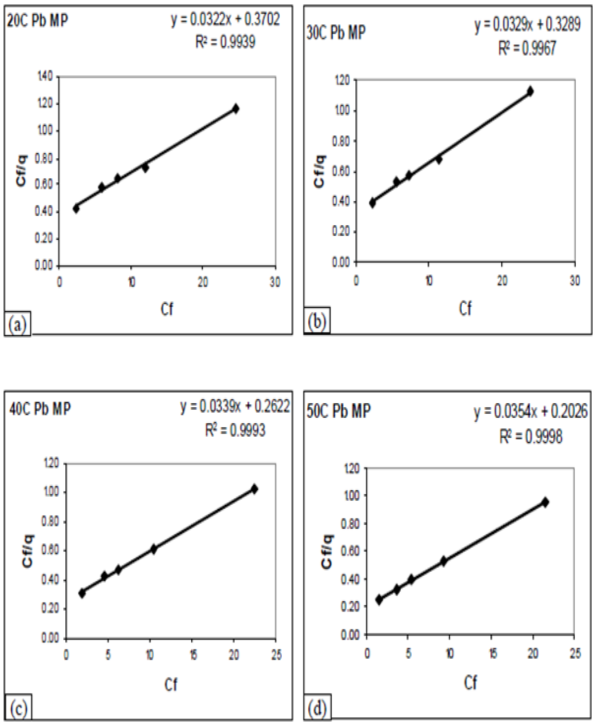

Fig 8. (a), (b), (c), (d) Langmuir plot for lead adsorption at 20,30, 40 and 50^{oC}

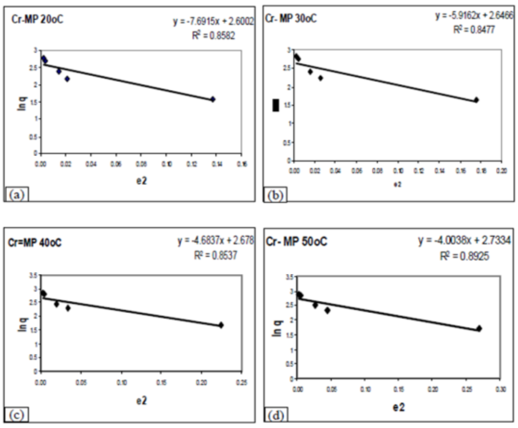

Fig 9. (a), (b). (c), (d) Dubinin-Radushkevich plot for chromium adsorption at 20,30, 40 and 50oC

Table 1. Isotherm parameters for the adsorption of Cd(II), Pb(II) ,Zn(II),Cu(II) and Cr(III) onto Lemon peel

Heavy Metals	T(K)	R^2	Langmuir model q_{max}(mg/g)	b(Lmg^{-1})	Freundlichmodel R^2	1/n	K	Dubinin-Radushkevich R^2	q_{max}(mg/g)	E(kJmol^{-1})
Cd(II)	293	0.995	15.08	0.241	0.866	0.251	5.68	0.996	13.40	0.466
	303	0.999	16.72	0.384	0.979	0.226	7.23	0.928	14.63	0.815
	313	0.999	16.67	0.751	0.940	0.179	8.92	0.899	14.97	1.698
	323	0.999	17.30	0.992	0.966	0.172	9.76	0.944	15.95	0.910
Pb(II)	293	0.994	31.05	0.086	0.982	0.579	3.55	0.839	16.29	0.561
	303	0.996	30.40	0.110	0.977	0.565	3.87	0.848	16.65	0.614
	313	0.999	29.50	0.129	0.973	0.532	4.58	0.853	16.95	0.748
	323	0.999	28.25	0.175	0.961	0.496	5.42	0.885	17.64	0.889
Zn(II)	293	0.993	23.47	0.053	0.980	0.627	1.69	0.962	14.42	0.377
	303	0.995	24.50	0.058	0.987	0.617	1.89	0.953	15.03	0.430
	313	0.993	24.57	0.069	0.989	0.597	2.19	0.948	15.53	0.505
	323	0.993	25.25	0.086	0.991	0.565	2.68	0.926	16.16	0.629
Cu(II)	293	0.991	15.30	0.175	0.892	0.284	4.69	0.922	12.33	0.536
	303	0.995	16.00	0.183	0.883	0.297	4.75	0.945	12.95	0.535
	313	0.998	16.13	0.216	0.844	0.285	5.15	0.968	13.58	0.584
	323	0.998	16.40	0.256	0.831	0.276	5.55	0.975	14.13	0.666
Cr(III)	293	0.991	24.80	0.039	0.980	0.561	1.88	0.858	13.46	0.255
	303	0.994	24.39	0.047	0.994	0.540	2.18	0.847	14.10	0.291
	313	0.995	24.69	0.052	0.991	0.529	2.43	0.854	14.52	0.326
	323	0.999	23.90	0.065	0.975	0.518	2.63	0.892	15.38	0.353

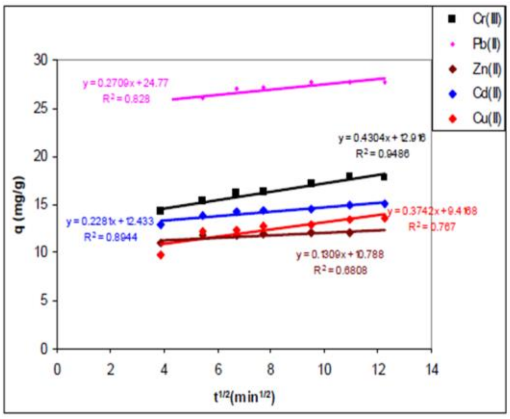

Fig 10. Plots for evaluating intra particle diffusion rate constant

3.6. Characterization of the adsorbent

To determine the distinct functional groups contained in a sample, a Fourier transform infrared spectral analysis was used. The samples supplied contain the various functional groups OH stretching, CH stretching, C=C stretching, and C-O stretching. According to the FT-IR spectra of the raw mango peel sample provided, the stretching of the O-H group caused by intra- and intermolecular hydrogen bonding of polymeric substances like alcohols or phenols was responsible for the broad and intense peak at 3345.5cm-1. The stretching vibrations of the CH bonds in the methyl, methylene, and methoxy groups were responsible for the peak at 2918 cm-1.

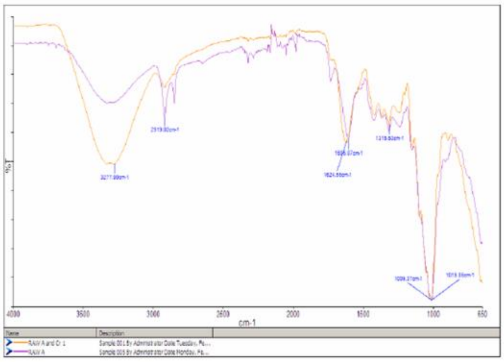

Fig 11. FTIR spectra before and after metal ion adsorption on chromium

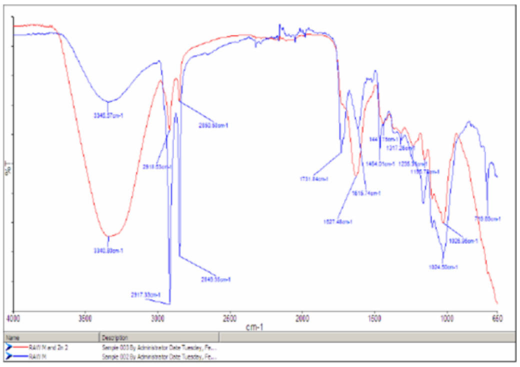

Fig 12. FTIR spectra before and after metal ion adsorption on zinc

IV. CONCLUSION

According to this study, mango peel may be used as an effective biosorbent material to remove Cd(II), Pb(II), Zn(II), Cr(III), and Cu(II) from wastewater. Mango peel is readily available and inexpensive. The Langmuir Freundlich and Dubinin-

Radushkevich isotherm models could provide a good description of the adsorption isotherms at various temperatures. 0.1 N HCl was found to be an effective desorbent in desorption studies for recovering Cu(II), Pb(II), and Zn(II) from biomass. According to IR spectrum analysis, the presented samples contain various functional groups including OH stretching, CH stretching, and C=C stretching-O stretching.

Thermodynamic analysis demonstrates the endothermic nature of the adsorption of Cd(II), Pb(II), Zn(II), Cr(III), and Cu(II). The process is feasible and spontaneous, as shown by the negative values of G.

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