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Adsorption of Cd(II) ions from aqueous solution using fruits peel as cost effective adsorbents

Swarnabala Jena
College of Basic Science & Humanities, OUAT, Bhubaneswar, India
E-mail: swarnajena.chem@gmail.com

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The adsorption of cadmium ion onto different fruits peel i.e lemon, orange and banana has been investigated by batch adsorption process with the variation in the *p*H, metal ion concentration, adsorbent dose and contact time. The results showed maximum removal efficiency of 94.7%, 98.4%, and 83.6% for banana, lemon and orange respectively. Freundlich and Langmuir adsorption isotherm models have been applied. Langmuir adsorption isotherm model is best fitted in the adsorption showing monolayer adsorption of Cd(II) ion. Pseudo first order and second order kinetics were applied showing higher r^2 values for second order kinetics. Pseudo-first order rate constant (k_1) for lemon, banana and orange are 0.1384, 0.1387, and 0.1451 whereas Pseudo-second order rate constant (k_2) for lemon, banana and orange are 0.857, 0.808 and 0.738 respectively.

Keywords: Adsorption, Fruits peel, Langmuir adsorption isotherm, Monolayer adsorption, Pseudo first order and second order kinetics

The discharge of heavy metals along with industrial effluents into the water builds is one of the most serious anxieties now days. The presence of heavy metals in industrial wastewater causes severe environmental along with community health distresses[1]. The carcinogenic properties of these heavy metals cause serious ecological threat and hazardous to manhood, livestock and the aquatic environment[2,3]. Numerous metals which are considerably toxic to humans and environment include Cu, Pb, Cd, Zn, Ni, Hg etc. Out of which Cadmium is most toxic heavy metal[4] which find its way to the water bodies through industries like metal production, phosphate fertilizers, pesticides, electroplating, textile operations, mining, refining processes, manufacture of batteries and pigments and dyes[5,6]. Cadmium toxicity causes a number of acute and chronic disorders such asitai-itai disease, renal damage, emphysema, hypertension, testicular atrophy, damage to the kidneys, lungs and liver, carcinogenesis etc.[7]. Hence, for safety of environs the maximum concentration limit for cadmium ion in drinking water has been firmly controlled by different groups. According to World Health Organization (WHO) the maximum permissible limit for Cd (II) in drinking water is of 0.003 mg/L[8]. Therefore there is great interest for scientist to remove cadmium from industrial waste water streams for very low concentrations. Numerous treatment methods for the removal of cadmium ions from waste water streams have been widely used by many researchers. But firm environmental protection regulation and civic environmental concerns lead the search for novel techniques to remove heavy metals from industrial waste water. Some widely used treatment methods include reverse osmosis, electro dialysis, ultra-filtration, ion exchange, chemical precipitation, phytoremediation etc.[9]. However, less efficiency, time consuming, disposal, high operational cost and input of chemicals often make these processes impractical and results in further environmental damage[10]. Hence, it is essential to treat industrial effluent with sorbents which are simple, comparatively inexpensive and eco-friendly than commercial activated carbon. Biosorption is a simple, most efficient and cost effective technique based on the principle of metal binding capacities of various biological materials and useful process for removal of heavy metals from wastewater[11-14]. Therefore there is real need for suitable and relatively cheap biosorbents that are capable of removing substantial quantities of heavy metals from waste water. The biological wastes, both dead and live biomass exhibit interesting metal-binding capacities. The use of dead biomass removes the problem of toxicity and the economic aspects of nutrient supply and culture maintenance[15]. A variety of adsorbents, including rice husk[16,17], ulmus leaves and ulmus leaves ash[18], banana peel[19], mangos teen shell[20], brown alga[21], loquat leaves[22], orange waste[6], coconut shell powder[15], coconut coprameal[23], nanozerovalent iron particles[24], olive stones[25], dried sludge[26], fungi-Aspergillus niger[27], sugarcane bagasse[28], pomelo peel[29], clays, zeolites, activated carbon have been used for cadmium removal. The fruits peel has strong adsorbing potential due to large surface area to volume ratio and high binding affinity to pollutants. The cell walls of the adsorbent are porous and allow the free passage of metal ions in aqueous solution[30]. They contain high contents of cellulose, pectin (galactorin acid)[31], hemicelluloses, lignin and citruline, those bear polar functional groups like carboxylic acid, phenolic acid and amino acid, responsible for binding the metal ions.

In this study, different fruit peels i.e. Orange, lemon and banana have been subsequently used to treat the Cd (II) ion concentration from aqueous solution. The effect of *p*H, contact time, adsorbent dose and effect of concentration were measured. Frendulich and Langmuir isotherm models are applied to the results. The results are also applied to pseudo first and second order kinetic models.

Experimental Section

All the chemicals and reagents used were of analytical reagent (AR) grade. Double distilled water was used for all experimental work including the preparation of metal ion solutions. The desired *p*H of the metal ion solution was adjusted with the help of 0.1N HCl and/or 0.1N NaOH.

Preparation of Cd (II) ions solution

A stock solution of cadmium (1000 ppm) was prepared by dissolving 2.744g of cadmium nitrate (Sigma-Aldrich) in 1 litre of double distilled water. Standard solutions of the desired concentrations (10–80ppm) were prepared by successive dilutions of the stock solution.

Preparation of adsorbent

Orange, Banana, Lemon fruits were purchased from a local market of Bhubaneswar city and peeled off manually. The peels were washed thoroughly with distilled water to remove the dirt and sundried for 5-7 days and then oven dried at 50-60°C.The dried fruit peels were crushed by mechanical blender and sieved to obtain a particle size of 0.355 mm and used as such[32].

Equipment and apparatus

The *p*H of the solution was measured by systronics digital *p*H meter-335. For shaking purposes rotating shaker of DBK Instrument, 28 interlink was used. Cadmium content in each experiment was measured by flame atomic absorption spectrophotometer (Perkin-Elmer-A Analyst-200). FTIR spectroscopy (JASCO-410 model) was used to identify the functional group present in the adsorbent. Scanning electron microscope of ZEISS (JEOL-JSM-6510) was used for determining the surface morphology of adsorbent. WENSAR™ Electronic balance was used for measuring the weight of adsorbent.

Batch adsorption studies

The static method was applied for adsorption of cadmium ions onto different fruit peels as a function of initial *p*H, contact time, adsorbent dosages, and contact time at temperature 30°C. All the experiments were carried out in 250 mL reagent bottle with agitation speed of 150 rpm for 2 hours. Whatmann-40 filter paper was used for filtering the contents after adsorption and the amount of Cd (II) ions after adsorption was determined using Atomic Adsorption Spectroscopy (AAS). The following equation was used to compute the percentage adsorption of Cd (II) ions by the adsorbent.

$$\text{Adsorption}(\%) = \frac{C_o - C_e}{C_o} \times 100$$

Where, C_o is the initial metal ion concentration in mg/L, and C_e is the metal ion concentration at equilibrium in mg/L.The equilibrium cadmium (II) ions adsorptive quantity was determined by the following equation:

$$q_e = \frac{(C_o - C_e)V}{W}$$

where q_e (mg/g) is the amount of cadmium (II) ions adsorbed, V (in litre) is the solution volume and w (in gram) is the amount of dry biosorbent used.

Results and Discussion

Effect of *p*H

The effect of *p*H has been studied by varying it on the range of 2-8 at 30°C with 50 mL of 10 ppm Cd (II) solution, adsorbent dose 1g, contact time 2h and agitation speed 150 rpm. The amount of adsorption and percentage of adsorption were shown in Table 1. Figure 1 shows the % of removal of cadmium ion at different *p*H. It is observed the removal of Cd (II) increases with increase of *p*H. The adsorption maximum was observed at *p*H 8 with removal efficiency of 94.7, 98.4, and 83.6% for banana, lemon

Table 1 — Amount and % of adsorption of the adsorbent at various *p*H

*p*H	q_e(mg/g)			% Adsorption		
	Banana	Lemon	Orange	Banana	Lemon	Orange
2	0.283	0.320	0.244	56.7	64.1	48.8
3	0.354	0.401	0.272	70.8	80.3	54.4
4	0.378	0.438	0.285	75.7	87.6	57
5	0.428	0.474	0.305	85.6	94.9	61.1
6	0.462	0.489	0.361	92.4	97.9	72.2
7	0.471	0.490	0.372	94.2	98.1	74.4
8	0.473	0.492	0.418	94.7	98.4	83.6

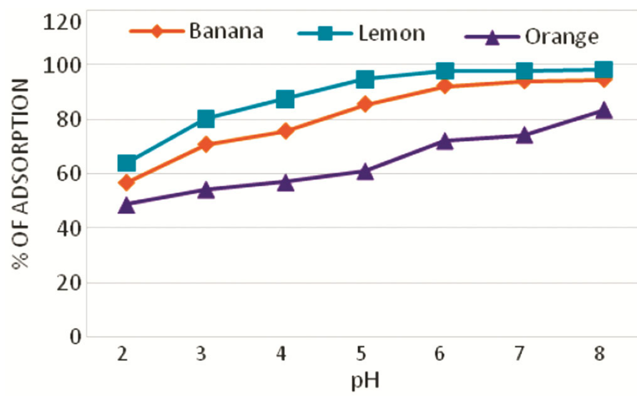

Fig. 1 — Effect of *p*H on the Cd (II) removal.(50 ml 10 ppm Cd (II) solution adsorbent dose 1g, contact time 2 hrs, agitation speed 150 rpm)

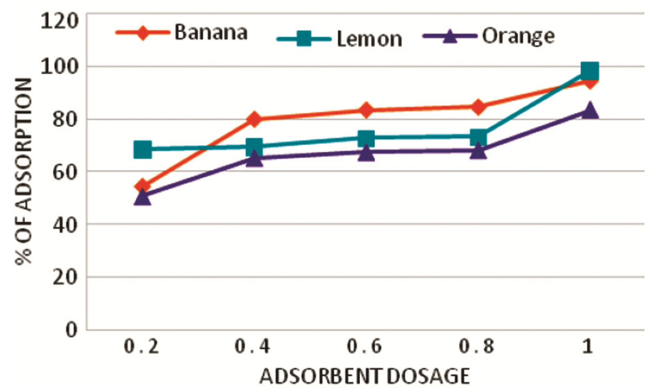

Fig. 2 — Effect of adsorbent dose on the Cd (II) removal. (50 mL 10 ppm Cd(II) solution, *p*H 8, contact time 2 h, agitation speed 150 rpm)

and orange respectively. The maximum adsorption capacities at different *p*H were 0.473, 0.492 and 0.418 mg/g for banana, lemon and orange respectively. These observations can be explained by the fact that, at highly acidic *p*H, the overall surface charge on the active sites became positive and metal cation and protons compete for binding sites on cellwall, which results in lower uptake of metal[33]. As *p*H increases more ligands such as amino, phosphate and carboxyl groups would be exposed and carry negative charges with subsequent attraction of metal ions[34-36].

Effect of adsorbent dose

The effect of adsorbent dose on adsorption of Cd was studied using different dosage in the range 0.2 to 1 g/50 mL and shown in Fig. 2. Results showed that the adsorption efficiency is highly dependent on quantity of adsorbent added. Maximum % of removal was 94.7, 98.4, and 83.6% and maximum adsorption capacities were 1.367, 1.712 and 1.270 mg for banana, lemon and orange respectively (Table 2). The adsorption increases with increase of adsorbent dose. Increase in adsorption by increase in adsorbent dose is because of increase of ion exchange site ability, surface area and the number of available adsorption sites[37].

Effect of initial Cd (II) ion concentration

The effect of initial Cd (II) ion concentration on various adsorbents was studied at 30°C temperature by varying the concentration of cadmium ion from 10 ppm to 80 ppm at adsorbent dose of 0.2 g/50 mL and *p*H 8.0. The maximum adsorption capacities are 1.712, 1.557 and 1.466 mg/g and maximum % of removal is 68.5, 62.3 and 58.67% for lemon, banana and orange respectively (Table 3). Analysis of % adsorption versus initial varying concentration of Cd (II) ions showed that the % adsorption decreased with increase in initial concentration (Fig. 3) of the adsorbate but the uptake capacity increased with increase in initial concentration. At the lower concentrations of cadmium ions, the number of Cd (II) ions which are available in the solution is less as compared to the available sites on the adsorbent. However, at the higher concentrations, the available sites for adsorption become fewer and the % removal of cadmium ions depends on the initial concentration[38].

Effect of contact time

Contact time plays an important role in affecting efficiency of adsorption. Contact time is the time needed for adsorption process to achieve equilibrium

Table 2 — Amount and % of adsorption of the adsorbent at various doses

Adsorbent dosage	q_e(mg/g)			% Adsorption		
	Banana	Lemon	Orange	Banana	Lemon	Orange
0.2	1.367	1.712	1.270	54.7	68.5	50.8
0.4	1.002	0.870	0.816	80.2	69.6	65.3
0.6	0.697	0.606	0.562	83.7	72.8	67.5
0.8	0.530	0.457	0.426	84.8	73.2	68.2
1.0	0.473	0.492	0.418	94.7	98.4	83.6

Table 3 — Amount and % of adsorption of the adsorbent at various concentrations

Concentration	q_e(mg/g)			% Adsorption		
	Banana	Lemon	Orange	Banana	Lemon	Orange
10	1.557	1.712	1.466	62.3	68.5	58.7
20	2.510	2.700	2.543	50.2	54.0	50.9
40	4.260	3.590	3.684	42.6	35.9	36.8
60	5.270	4.422	4.885	35.1	29.5	32.6
80	7.160	5.865	4.305	35.8	29.3	21.5

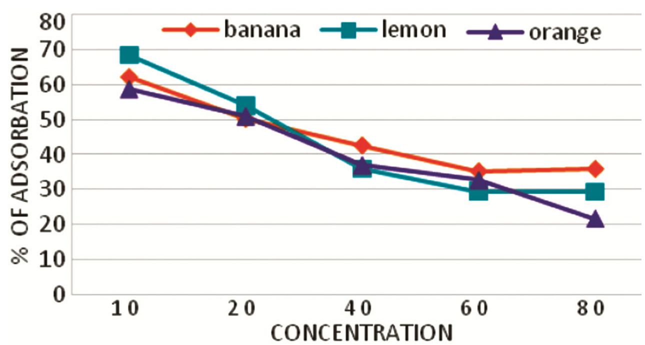

Fig. 3 — Effect of Cd (II) ion concentrations on the Cd (II) removal. (50mlCd(II) solution, *p*H 8, adsorbent dose 0.2g, contact time 2 h, agitation speed 150 rpm)

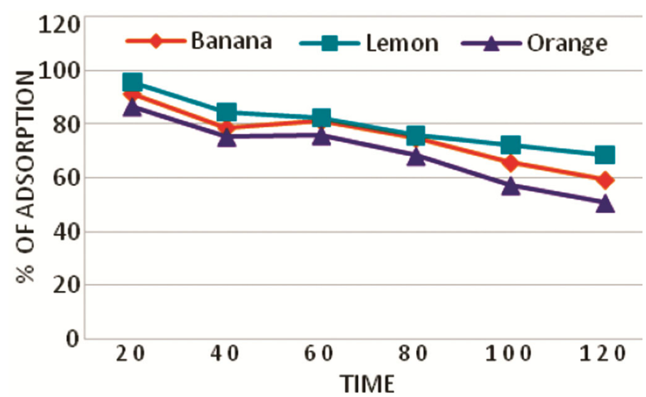

Fig. 4 — Effect of contact time on the Cd (II) removal. (50 mL 10 ppm Cd (II) solution, *p*H 8, adsorbent dose 0.2g,agitation speed 150 rpm)

when no more changes in adsorptive concentration were observed after a certain period of time. In order to optimize the contact time for the maximum uptake of Cd(II) ions, contact time was varied between 20-120 min in the concentration of Cd(II) ions 10 ppm, adsorbent dose 0.2 gm/50 mL, optimum *p*H 8.0 and 30°C temperature. The results showed that the biosorption capacity is high initially but with increase in time it decreases upto 60 min and after that removal efficiency decreases very slowly (Fig. 4). Initially there were large number of vacant active binding sites available at the first phase of experiment and large amount of the adsorbate were bound rapidly at a faster adsorption rate. The binding site was shortly become limited and the remaining vacant surface sites were difficult to be occupied by metal ions due to formation of repulsive forces between the cadmium on the solid surface and the liquid phase[19]. Highest uptake for lemon, banana and orange is 2.390, 2.282, 2.170 mg and maximum % removal are 95.6, 91.3, and 86.8% respectively (Table 4).

Adsorption isotherms

The experimental data were applied to the two-parameter isotherm models; Langmuir and Freundlich[14].

Langmuir adsorption isotherm

The Langmuir equation which is valid for monolayer sorption onto a surface of finite number of identical sites, is given by[39]

$$q_e = \frac{q_m b c_e}{1 + b c_e}$$

where "qm" the maximum biosorption capacity of adsorbent, "b" is the Langmuir biosorption constant (Lmg^{-1}) related to the affinity between the biosorbent and sorbate. Linearized Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constants and is represented as

Table 4 — Amount and % of adsorption of the adsorbent at various times

Time	q_e(mg/g)			% Adsorption		
	Banana	Lemon	Orange	Banana	Lemon	Orange
20	2.282	2.390	2.170	91.3	95.6	86.8
40	1.965	2.110	1.887	78.6	84.4	75.5
60	2.027	2.055	1.902	81.1	82.2	76.1
80	1.867	1.892	1.707	74.7	75.7	68.3
100	1.642	1.802	1.435	65.7	72.1	57.4
120	1.482	1.712	1.270	59.3	68.5	50.8

Table 5 — Langmuir, Freundlich isotherms and their constants

Isotherm and constants		Adsorbents		
		Lemon	Banana	Orange
Langmuir	q_m	0.20978	0.12976	0.17375
	b	41.1523	37.1341	26.2667
	R_L	0.00030	0.00034	0.00048
	r^2	0.912	0.921	0.983
	θ	0.9997	0.9997	0.9995
Freundlich	K	1088.3	710.755	884.179
	1/n	0.56757	0.39211	0.42508
	r^2	0.990	0.983	0.920

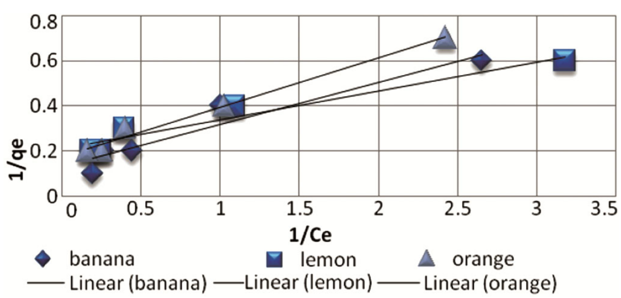

Fig. 5 — Langmuir adsorption isotherms

$$\frac{1}{q_e} = \frac{1}{q_m b c_e} + \frac{1}{q_m}$$

The linear plot of $\frac{1}{q_e}$ Vs $\frac{1}{C_e}$ is shown in Fig. 5. Two constants b and q*m* are calculated from the slope $\frac{1}{q_m b}$ and intercept $\frac{1}{qm}$ of the line.

The values of q_m, b and regression coefficient (r^2) are listed in Table 5. Maximum biosorption capacity of adsorbent (q_m) is found to be 0.20978 mg/g, 0.17375 mg/g, 0.12976 mg/g for lemon, orange and banana respectively. The essential features of Langmuir isotherm can be expressed in terms of a dimensionless constants or separation factor or equilibrium parameter (R_L) and expressed as in the following equation[40,41].

$$R_L = \frac{1}{1 - bc_i}$$

Where 'b' is the Langmuir constant and 'c_i' is the maximum initial concentration of Cd (II) ions. The R_L value provides important information about the nature of adsorption. There are four probabilities for the R_L value

1) for favorable adsorption $0 < R_L < 1$
2) for unfavorable adsorption $R_L > 1$
3) for linear adsorption $R_L = 1$
4) for irreversible adsorption $R_L = 0$

The R_L value was found to be 0.00030, 0.00034 and 0.00048 for lemon, banana and orange respectively in the concentration range 10-80 ppm indicating favourable biosorption[42]. Biosorption can also be understood in terms of surface area coverage against initial metal ion concentration and separation factor. Langmuir model for surface area of biosorbent surface has been represented as follows

$$bc_i = \frac{\theta}{1 - \theta}$$

Where 'θ' is the surface area coverage. The value of 'θ' was found to be 0.9995, 0.9997 and 0.9997 for orange, lemon and banana respectively. The 'r^2' values for lemon, banana and orange are 0.912, 0.921 and 0.983 respectively, which shows there is a good correlation exists between the pairs of parameter ($1/q_e$vs $1/c_e$) in Langmuir equation.

Freundlich adsorption isotherm

Freundlich equation is represented by

$qe = Kc_e^{1/n}$, where 'K' and 'n' is empirical constant. Linearized Freundlich adsorption isotherm[43] was used to evaluate the sorption data and is represented as

$$\text{Log}q_e = \log K + \left(\frac{1}{n}\right) \log c_e$$

Equilibrium data for the adsorption is plotted as log q_e vs log c_e as shown in Fig. 6. The two constants n and K are calculated from the slope $\left(\frac{1}{n}\right)$ and intercept (log K) of the line respectively.

The values of K, 1/n and regression coefficient (r^2) are listed in Table 5. "1/n" values were found to be 0.56757, 0.39211, and 0.42508 and "r^2" values were 0.990, 0.983 and 0.920 for lemon, banana and orange respectively shows good correlation between the pairs of parameters. The magnitude of K and 1/n shows informal separation of Cd (II) ion from water solution and high adsorption capacity. The value of 1/n, which is related to the distribution of bonded ions on the adsorbent surface represents, useful adsorption if it is in between 0.1 and 1. The 1/n values of the adsorbents are indicating that the adsorption of Cd (II) is favourable. The 'K' values for lemon, banana & orange are found to be 1088.3, 710.755 & 884.179 respectively. The higher value of 'K' indicates the higher adsorption capacity of the adsorbent.

SEM and FTIR analysis

The SEM and FTIR images of the adsorbents before loaded cadmium were given in our previous work report[44]. According to the report, SEM images of banana shows agglomeration of surface showing poor adsorption compare to lemon and orange peel surface. Orange shows some needle like structure so the efficiency to bind metal ions is reduced in compare to lemon. More porous surfaces in lemon could promote the adherence of cadmium. The exposure and availability of binding sites depends on particle shapes and sizes of adsorbent[45]. FTIR spectral reports in our previous study[44] before loaded cadmium ion showed that the bands at 3321 cm^{-1} correspond to O-H (hydroxyl), between 2906-2936 cm^{-1} is $C\text{-}H_{str}$, 1607-1617 cm^{-1} is carboxyl, 1048-1057 cm^{-1} is O-H bend (ester). SEM images showed the surface of lemon is highly porous which easily loaded cadmium metal ions to its surface.

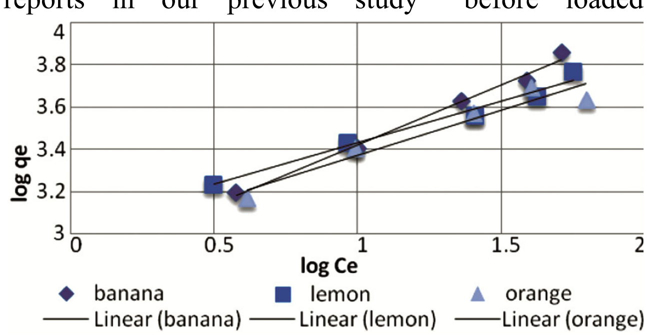

Fig. 6 — Freundlich adsorption isotherm

The broad and intense peak around 3294 cm^{-1} corresponds to –OH stretching vibrations containing cellulose, absorbed water, hemicelluloses, pectin and lignin. Peaks at 2918 cm^{-1} corresponds to –CH stretching vibrations of methyl and methoxy group. Peaks between 1602-1419 cm^{-1} corresponds to –C=O stretching of carboxylic acid or esters. Peak at 1025 cm^{-1} is assigned to stretching vibrations of carboxylic acid and alcohols. The spectrum shows carboxylic and hydroxyl groups are present in abundance and these groups act as proton donor and coordinated with metal ions.

Adsorption kinetics

The Lagergren's pseudo-first order and pseudo-second-order models were performed to the experimental data to clarify the adsorption kinetics of Cd (II) ion onto fruits peel.

Pseudo-first order kinetic model

The experimental data was fitted with the linear form of the pseudo-first order rate equation by the Lagergren[46] given as

$$\text{Log}(q_e - q_t) = \text{Log}\, q_e - \frac{K_2}{2.303} t$$

Where q_e (mg/g) is the solid phase concentration at equilibrium, q_t (mg/g) is the average solid phase concentration at time't' (min). k_1 (min^{-1}) is the pseudo-first order rate constant.

The adsorption follows the pseudo-first order rate equation and a plot of log (q_e-q_t) against time't' shows a straight line. The value of q_e and K_1 were calculated from the slope and intercept of the plot. The pseudo-first order kinetic model showed the correlation values (R^2) 0.859, 0.887, 0.876 for lemon, banana and orange respectively. The equilibrium rate constants (k_1) for lemon, banana and orange were 0.1384, 0.1387, and 0.1451 respectively. Table 6 shows the adsorption kinetic data for biosorption of Cd (II) by different fruit peels. From the table it is observed that, there is hardly any change in the value of rate constant at various adsorption parameters and adsorption data fitted well in first order kinetic model.

Pseudo-second order kinetic model

The pseudo-second order kinetic model is given in the following form[47]

Table 6 ─ Pseudo-first and second order kinetics and constants

Kinetics & constants		Lemon	Orange	Banana
Pseudo-first order	k_1	0.1384	0.1451	0.1387
	q_e	1.4425	0.3278	0.2175
	R^2	0.859	0.876	0.887
pseudo-second order	k_2	0.857	0.738	0.808
	q_e	2	1.7	1.8
	R^2	1.00	1.00	1.00

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

Where k_2 (g/mg min) is the rate constant of the second order equation, q_e and q_t are the amount of adsorption at time 't' and the average solid phase concentration at time 't' respectively. The plot of 't/q_t' Vs 't' gives a linear relationship from which q_e and k_2 are calculated. The kinetic data are listed in Table 6.

The rate constant is 0.857, 0.738 and 0.808 for lemon, orange and banana respectively. From the Table it can be seen that the R^2 of the pseudo-second order kinetic model for Cd (II) is high i.e. 1.000 which shows strongest correlation. It can also be found from Table 6 that q_e values for the pseudo-second order kinetic model are very high than pseudo-first order kinetic model. The constancy of rate constant values shows the data fitted well in second order kinetics than first order. The correlation coefficient values (R^2) for pseudo-first order model is lower than the values of pseudo-second order kinetic model. This indicates kinetic adsorption for pseudo-first order model occurs chemically and involves valence forces through ion sharing or exchange of electron between the adsorbent & the ions adsorbed onto it[48]. But the pseudo-second order model suggest that Cd(II) ions adsorption occurs in a monolayer fashion and which relies on the assumption that chemisorption is the rate limiting step. Cd (II) ions react chemically with the specific binding sites on the surface of biosorbent.

Conclusion

The present investigation reveals that fruit peels are inexpensive, excellent biosorbent for the removal of Cd (II) ions from aqueous solutions. The optimal parameters viz. solution *p*H, adsorbent dose, initial Cd(II) ions concentration, contact time determined in the experiment were effective in determining the efficiency of Cd(II) ions onto fruit peels. The maximum Cd (II) ion loading capacity for lemon was found to be 0.2097 mg/g with perfect fit to Langmuir adsorption isotherm model and follows pseudo-second order kinetics. Batch adsorption studies showed that lemon acts as excellent sorbent than banana and orange with maximum removal efficiency of 98.4% at *p*H 8 and 30°C temperature. From these observation it can be concluded that lemon has considerable biosorption capacity, available in abundant, non-hazardous agrowaste material could be used as cost effective material for treatment of industrial waste water containing Cd (II) ions.

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