Removal of Cd^{2+} from synthetic solution by using leaves of Neem, Peepal and Mixed adsorbent

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ABSTRACT

In this study, two adsorbents Neem and Peepal were prepared from the leaves of *Azadirachta indica* (Neem) and *Ficus religiosa* (Peepal). During batch studies, four parameters i.e., pH, adsorbent dose, contact time and initial metal ion concentration were studied. It was observed that the optimum pH, adsorbent dose, contact time and initial metal ion concentration for Neem were 9, 0.14g/50ml, 120 minutes, and 5 mg/l respectively. For Peepal, the optimum pH, adsorbent dose, contact time and initial metal ion concentration were 9, 0.12g/50ml, 80 minutes, and 5 mg/l respectively. For Mixed adsorbent, the optimum pH, adsorbent dose, contact time and initial metal ion concentration were observed 9, 0.10g/50ml, 160 minutes, and 5 mg/l respectively. The Freundlich adsorption isotherm was well fitted than Langmuir adsorption isotherm in all cases.

Keywords: Adsorbent, Freundlich adsorption isotherm, Langmuir adsorption isotherm.

INTRODUCTION

In recent decades, population, urbanization and industrialization kept on increasing exponentially and reached at an alarming level. The industrialization has led to generation of untreated industrial waste water that carries toxic contaminants including heavy metals. The heavy metal pollution in terrestrial and aquatic environment is one of the major concerns throughout the world (Jain *et al.*, 2014).

This pollution is endangering the environmentand making direct effect on flora and fauna due to its toxicity, carcinogenicity, persistence behavior and also may cause mutation in genetic material. Besides this, it may alsocause health issues like hemolysis, gastroenteritis, nervous system, skin, liver, reproductive and urinary disordersetc. (Lobo &Gulimane, 2015).

Cadmium is one of the heavy metals with extensive usage and finds its way in our water resources and causes adverse health effects. Several treatment processes for the removal of cadmium from aqueous solutions have been reported like ion exchange, solvent extraction, reverse osmosis, chemical precipitation, membrane filtration and adsorption(Kovo *et al.*, 2014).But the above discussed methodshave significant disadvantages and are quite expensive and not eco-friendly. On the other hand, adsorption through agricultural products such as rice husk, sugarcane bagasse, banana peels, soybean hulls, papaya peels, saw dust, coconut shell, gulmohar's fruit shell, groundnut shell, apple waste, mangrove leaf powder, fly ash etc., has been demonstrated as a useful alternative to the conventional treatment systems (Parlayici & Pehlivan, 2019). This is considered as an eco-friendly device to the existing relatively more expensive treatment technologies (Kaya *et al*., 2014).

MATERIAL AND METHODS

Preparation of Neem and Peepal Adsorbents

The leaves were obtained from Neem tree (Azadirachta indica) and *Ficus religiosa*(Peepal). Carbon based adsorbents from mature leaves of Neem and Peepal were prepared to investigate their potential for the removal of Cadmium(II) from synthetic samples.All chemicals and reagents were used of A.R.grade.Fresh leaves were chosen based on their crude fiber content. They were sun dried for 3-4 days and crushed manually. Leaf powder was further digested by chemical method taking leafpowder (40g) and 400 ml of 0.2N HNO_3(nitric acid) in a 1000 ml conical flask. The mixture was gently heated on burner for 20 minutes after boiling started. Treated biomass was washed off with distilled water. Washing was done until maximum color was removed and clear water obtained. The sample was further washed with 1% sodium bicarbonatesolution to neutralize the traces of acid and again washed with distilled water. The dried powder was sieved to 0.125 mm pore size and the adsorbents were stored in airtight bottle. For mixed adsorbent, both Neem and Peepal adsorbents were mixed in 1:1 ratio.

Preparation of synthetic solution of cadmium (II)

A stock solution of 1000 mg/l of cadmium(II) synthetic solution was prepared by dissolving 1.3535 g of $CdCl_2$in 5ml of concentrated HNO_3 and then diluted to 1000 ml. Cadmium(II) was determined spectrophotometrically. A calibration curve for Cd (II) was formed between absorbance and standard Cd (II) solution of various strength.

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Uptake studies in batch process

Adsorption studies were performed by batch technique to obtain the rateand equilibrium data. Experiments were carried out by shaking 0.1g of adsorbent dose with 50 ml of aqueous solution containing known concentration 10 mg/l of cadmium ions and by agitatingthe samples for 60 minutes on shaker (Remi) at a speedof 180 strokes/min. All the experiments were conducted at room temperature (25 ± 0.5°C).After filtration, 10 ml was taken in a 25ml conical flask and to it 2.5 ml citrate buffer, 0.024 % pyronin G, 10% KIeach and 1ml 1% gelatin were added. Then the filtrates were analyzed for Cd (II) concentration at 575nm spectrophotometrically.The amount of Cadmium adsorbed was determined by mass balance according to the following equation:

$$\%\ \text{Removal of Cd(II)} = \frac{C_{(\text{initial})} - C_{(\text{final})}}{C_{(\text{initial})}} \text{x}100$$

Where $C_{(initial)}$ is initial concentration of Cd, and $C_{(final)}$ is final concentration of Cd.

In this study,effect of different operating conditions-pH, adsorbent dose, contact time and initial metal ion concentration were optimized. The parameters were varied as pH from 6.0 to 10.0, adsorbent dose from 0.02 to 0.20g/50ml, contact time from 20 to 200minutes and initial metal ion concentration from 5 to 25 mg/l. The equilibrium adsorption with Freundlich and Langmuir isotherm models were analyzed.

RESULT & DISCUSSION

Adsorption of metal cations on adsorbent depends upon the nature and species distribution of metal cationson adsorbent surface, speciation on adsorbate, degree of ionization and electrostatic interaction between adsorbent and adsorbate (Farnane *et al*., 2018).

Many studies have shown that pH plays an important role between sorption of metal ions and magnitude of negative ions/ functional groups on surface of adsorbent. From batch experiments, optimum pH was found to be 9 for neem, peepal and mixed adsorbent, at which Cd(II) ion removal efficiency was 64.73%, 60.14% and 64.11% respectively. At the optimum pH, the sorbent surface takes more negative charges, thus attracting greater metal ions.At low pH, hydrogen ions are more preferentially adsorbed due to more Hydrogen ion concentration and high mobility of ions. (Adrian*et al.*, 2015).

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The optimum dose of adsorbents was found 0.14g/50ml with 66.72% Cd removal for neem, 0.12g/50ml with 63.14% Cd removal for peepal and 0.10g/50ml with 64.11% Cd removal for mixed adsorbent.The increase in adsorption by increasing the amount of the adsorbent is an effect of increase in adsorption sites.Further, the adsorbent sites decreased with increasing adsorbent dose due to reduction inmetal ions to binding sites ratio (Dwivedi *et al.,* 2014).

In case of contact time parameter, it was observed that adsorption was maximum at the initial stages which became nearly constant while approaching equilibrium. Such type of behaviour was expected in batch process studies (Kovo*et al.*, 2014) The optimum time for Neem was observedto be 120 minutes with 68.58% removal of Cd(II), for Peepal, it was 80 minutes with 64.86% removal of Cd(II) and for mixed adsorbent 160 minutes with 66.84% removal of Cadmium (II).

It was observed that the adsorption decreased with increase in initial metal ion concentration of Cd(II) from 5 to 25 mg/l. The maximum adsorption was observed at 5 mg/l concentration for Neem,Peepal and Mixed adsorbent with 72.81%,69.08% and 70.57% removal of Cd (II) respectively. It may be attributed to the large surface area with availability of more active sitespresent in the beginning, so metal ions uptake was more. Further metal ion adsorption was reduced at higher concentration of Cadmium ions because of lack of sufficient number of active sites on the adsorbent(Khajavian *et al.,* 2019).

The process of adsorption by treated adsorbents followed Langmuir and Freundlich adsorption isotherm, which comprised statistical and empirical data estimated from Isotherm equation.

Langmuir Isotherm

Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent andeach of these sites is capable of adsorbing one molecule. Thus, the adsorbed layer will be single molecular thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The Langmuir equation is commonly written as

$$qe = Q_o bC_e / (1 + bCe)$$

where qe is the amount adsorbed (mg/g) and Ce is the equilibrium concentration of adsorbate(mg/l), Qo and b are the Langmuir constants related to capacity and energy of adsorption,respectively.The Langmuir constants b and Qo are calculated from the slope and intercept with Y-axis respectively.The plot for adsorption of Cd(II) Neem, Peepal and Mixed adsorbent is given in fig.1, fig.2 and fig.3 respectively. The calculation for Langmuir isotherm for Neem, Peepal and Mixed adsorbent is given in tab.2, tab.3 and tab.4 respectively.

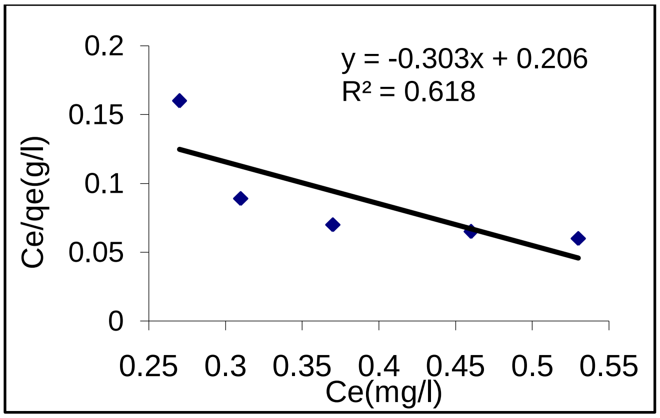

Fig. 1: Langmuir plot for adsorption of Cd(II) for Neem adsorbent

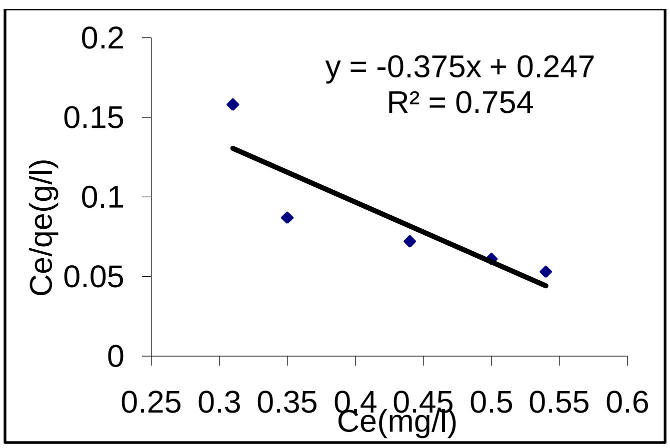

Fig. 2: Langmuir plot for adsorption of Cd(II) for Peepal adsorbent

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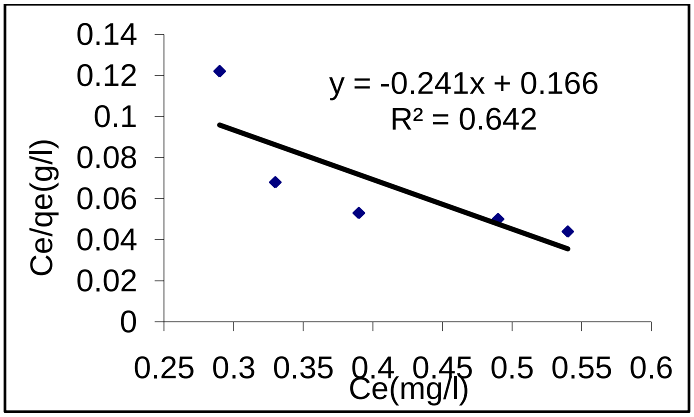

Fig. 3: Langmuir plot for adsorption of Cd(II) for Mixed adsorbent

Further, a dimensionless separation factor of Langmuir Isotherm, R_L is defined as

$R_L=1/1+bC_o$

Where, C_o = initial metal ion concentration.

The value of $R_L$indicates the feasibility of Langmuir adsorption. R_L values from 0-1 indicates favorable adsorption. If $R_L>1$ indicate unfavorable adsorption, $R_L=0$ shows irreversible adsorption (Mustapha*et al.*, 2019).R_L value for Neem, Peepal and Mixed adsorbent was observed maximum at 5mg/l cadmium ion concentration and between 0 to1indicating favorable adsorption as shown in tab.1.

Table 1: R_L values of different adsorbents

Conc. (mg/l) / **Adsorbent**	**5**	**10**	**15**	**20**	**25**
Neem	0.119	0.064	0.046	0.034	0.027
Peepal	0.116	0.061	0.042	0.031	0.026
Mixed	0.121	0.064	0.044	0.033	0.027

Freundlich Isotherm

It has the general form of

$$qe = K_f C^{1/n}$$

The linearised Freundlich adsorption isotherm, which is of the formlog

$$(qe) = \log K_f + 1/n \log Ce$$

where qe is the amount of metal ions adsorbed per unit weight of adsorbents (mg g^{-1}), K_f(intercept) and 1/n (slope) are theFreundlich constants, indicate adsorption capacity and adsorption intensity respectively (Farnane *et al*., 2018). The value of 1/n ranges between 0 to 1. Ce is the equilibrium concentration (mg/l). Linear plots of log qevs log Ce at different initial metal Cd(II) concentration were applied to confirm the applicability of Freundlich models for Neem, Peepal and Mixed adsorbent as shownin fig.4, fig.5 and fig.6 respectively.

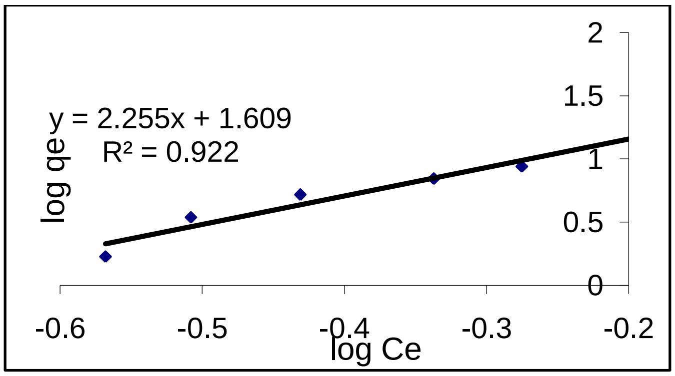

Fig. 4: Freundlich plot for adsorption of Cd(II) for Neem adsorbent

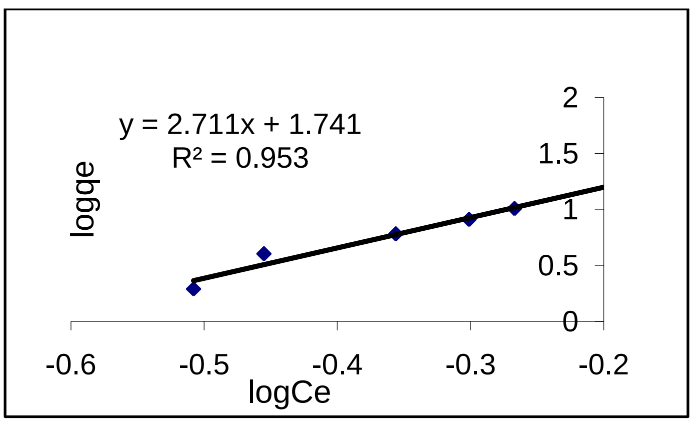

Fig. 5: Freundlich plot for adsorption of Cd(II) forPeepal adsorbent

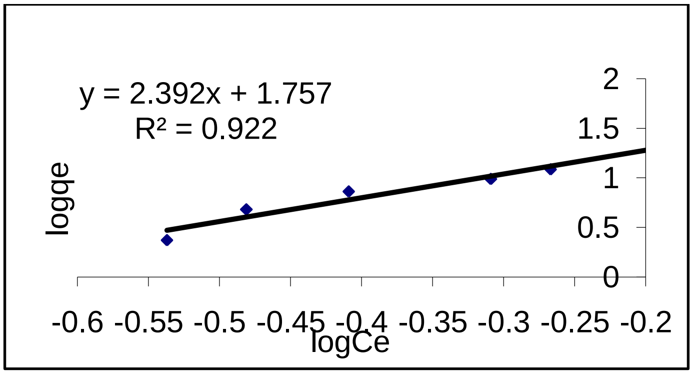

Fig. 6: Freundlich plot for adsorption of Cd(II) for Mixed adsorbent

Table 2: Calculation of Langmuir and Freundlich models for Neem adsorbent

Ci Initial Cd(II) ion conc. (mg/l)	Ce (mg/l)	qe (mg/g)	Ce/qe	log Ce	log qe
5	0.27	1.69	0.16	-0.568	0.227
10	0.31	3.46	0.089	-0.508	0.539
15	0.37	5.22	0.07	-0.431	0.717
20	0.46	6.97	0.065	-0.337	0.843
25	0.53	8.73	0.06	-0.275	0.941

Table 3: Calculation of Langmuir and Freundlich models for Peepal adsorbent

Ci Initial Cd(II) ion conc. (mg/l)	Ce (mg/l)	qe (mg/g)	Ce/qe	log Ce	log qe
5	0.31	1.95	0.158	-0.508	0.29
10	0.35	4.01	0.087	-0.455	0.603
15	0.44	6.06	0.072	-0.356	0.782
20	0.5	8.11	0.061	-0.301	0.909
25	0.54	10.18	0.053	-0.267	1.007

Table 4: Calculation of Langmuir and Freundlich models for Mixed adsorbent

Ci Initial Cd(II) ion conc. (mg/l)	Ce (mg/l)	qe (mg/g)	Ce/qe	log Ce	log qe
5	0.29	2.36	0.122	-0.537	0.372
10	0.33	4.83	0.068	-0.481	0.683
15	0.39	7.31	0.053	-0.409	0.863
20	0.49	9.76	0.05	-0.309	0.989
25	0.54	12.23	0.044	-0.267	1.087

Table 5: Isotherm constant for adsorption of Cd(II) for Neem, Peepal and Mixed adsorbent

Adsorbents	Langmuir isotherm			Freundlich Isotherm		
	Q_{max}(mg/gm)	**b(L/mg)**	**R^2**	**K_f**	**n**	**R^2**
Neem	3.29	1.47	0.62	40.65	5.56	0.92
Peepal	2.66	1.52	0.75	55.14	1.94	0.95
Mixed	4.14	1.46	0.64	57.16	4.05	0.92

*R^2 = Correlation coefficient

The values of Kf and n in Freundlich isotherm indicates thesystem of suitability with value n>1indicates the favorable adsorption condition. The value of n is greater in case of Neem in comparison to Mixed and Peepal adsorbent as shown in table 5.

The calculated values of correlation coefficient for both adsorbents showed that Freundlich isotherm is greater than Langmuir Isotherm in all three adsorbents Thus, Freundlich adsorption Isotherm was found more fitted than Langmuir adsorption Isotherm in all.

Conclusion

The analysis of results of present study indicated that these low-cost adsorbents may be fruitfully used for removal of cadmium (II). The optimum value of pH, adsorbent dose, contact time and metal ion concentration at which the maximum adsorption of cadmium ions was achieved. The process of adsorption by treated adsorbents followed Langmuir and Freundlich Adsorption isotherm, which comprised statistical and empirical data estimation from isotherm equation. The Freundlich adsorption isotherm was more fitted than Langmuir adsorption Isotherm. These adsorbents can be easily and safely disposed of and there is no need to regenerate as these are economical and easily available.

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REFERENCES

Adriana, Fachrialb, Edy., Almahdyc., Syaifullahd., Munafe., Edison., & Rahmiana Zein, Rahmiana. (2015). Biosorption of cadmium (II) ions from aqueous solution by cassava (Manihot utilissima) leaves. *Journal of Chemical and Pharmaceutical Research*, 7(9S), 1-8. ISSN: 0975-7384

ISSN- 2394-5125 VOL 7, ISSUE 01 , 2020

Dwivedi,Shubha., Mondal, Prasenjit., & Balomajumder, Chandrajit. (2014). Bioadsorption of Fluoride by Ficusreligiosa (Peepal Leaf Powder): Optimization of process Parameters and Equilibrium study. Res. J. Chem. Sci., 4(7), 52-60.

Farnane, M., Machrouhi, A., Elhalil, A., Abdennouri, M., S. Qourzal, S., Tounsadi, H., & Barka, N. (2018). New Sustainable Biosorbent Based on Recycled Deoiled Carob Seeds: Optimization of Heavy Metals Remediation. *Journal of Chemistry Volume*, Article ID 5748493, https://doi.org/10.1155/2018/5748493

Jain, R. N., Patil, S. B., & Lal, D.S. (2014). Adsorption of Cr-(vi) from aqueous environment using neem leaves powder. *International Journal of Research in Engineering and Technology,*3(9), ISSN: 2321-7308.

Kaya, K., Pehlivan, E., Schmidt, C., & Bahadir, M. (2014). Use of modified wheat bran for the removal of chromium (VI) from aqueous solutions. *Food Chem.,*158: 112–7.DOI: 10.1016/j.foodchem.2014.02.107

Khajavian, M., Wood, D. A., Hallajsani, A., & Majidian, Nasrollah. (2019). Simultaneous biosorption of nickel and cadmium by the brown algae Cystoseria indica characterized by isotherm and kinetic models. *Appl Biol Chem.,* 62-69. https://doi.org/10.1186/s13765-019-0477-6

Kovo, A. S., Olu, S. C., & Gwatana, E. S. (2014). Adsorption of Chromium (IV) by a lowcost adsorbent prepared from Neem leaves. *Iranica Journal of Energy & Environment*, 5(3), 277-286. ISSN: 2079-2115.

Lobo, S. M. & Gulimane, Krishnakumar. (2015). Biosorption of Heavy Metals from Aqueous solution using Mangrove fern Acrostichum aureum L. leaf Biomass as a Sorbent. *International Research Journal of Environment Sciences*. 4(11), 25-31. ISSN 2319–1414.

Mustapha, S., Shuaib, D. T., Ndamitso, M. M., Etsuyankpa, M. B., Sumaila, A., Mohammed, U. M., Nasirudeen, M. B. (2019). Adsorption isotherm, kinetic and thermodynamic studiesfor the removal of Pb(II), Cd(II), Zn(II)and Cu(II) ions from aqueoussolutions using *Albizia lebbeck* pods. *Applied Water Science*, 9:142. https://doi.org/10.1007/s13201-019-1021-x

ISSN- 2394-5125 VOL 7, ISSUE 01 , 2020

Parlayici,S., and Pehlivan, E. (2019). Comparative study of Cr(VI) removal by bio-waste adsorbents: equilibrium, kinetics, and thermodynamic. *J Anal Sci Technol* 10(15). https://doi.orApplied Water Science (2019) 9:142