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Removal of Pb (II) ions by Averrhoa carambola leaves from synthetic water. It's characterization and isotherm study.

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Abstract
Lead is one of the priority heavy metal due to its high degree of toxicity. It has many severe health implications on human as well as on the environment. In this research, potential of wastes leaves of Averrhoa carambolaas an adsorbent was experimented for the removal of Pb (II) ions from the synthetic water. Under various experimental conditions like contact time, pH, dose of adsorbent, initial metal ion concentration batch experiments were carried out. The maximum removal percentage was found to be 96%. The experimental data were fitted into Langmuir and Freundlich models. The results of the experiment reveal that the Pb (II) give best fit to Langmuir isotherm with r^2 value of .99. The optimum pH for the experiment was found to be 5 at 10mg/L metal ion concentration with dose of 2g and the equilibrium reached at 60 mins.The maximum capacity of the adsorbent was calculated from the isotherm models. The adsorbent was characterized usingBET (Brunauer–Emmett–Teller),pH.

Key Words: *Averrhoa carambola, Adsorbent, Batch, pH, Langmuir, Freundlich, BET,*

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I. Introduction

Developmental activities have resulted in heavy metal pollution around the globe. Various activities like mining, processing of metals, etc. are discharging heavy amount of metal loaded effluents into the environment. The heavy metal is defined as the elements having an atomic number greater than 20 and density above 5g/cubic centimeter. They must exhibit properties of metal also. The density of heavy metals is higher than water (Fergusson et al 1990) Heavy metals are toxic at low level of concentration. Because of high degree of toxicity, Lead have been categorized as priority heavy metals (Nagajyoti, et al, 2010) The maximum contamination level (MCL) value for lead in drinking water is .003mg/L (WHO,2019). Lead exists in two oxidation state (+2, +4) and has electronegativity of 2.33. The toxicity of heavy metals is a matter of serious concern from ecological, environmental causes (Tchounwou et al ,2012) There are various chemical methods available for removal of heavy metals from wastewater. The conventional methods for heavy metal removal from wastewater are membrane filtration, precipitation, coagulation. (Charerntanyarak, et al ,1999) This method has certain disadvantages as it generates sludge, consumes more energy, possess high operational cost. These drawbacks are overcome by application of natural adsorbent. The demand for natural adsorbent is high due to their many advantages. One of the important advantages of natural adsorbents is it can remove metal at low concentration also (Ahlaya et al ,2003). Lead is very toxic heavy metal in the environment. There are various sources of the lead. The industrial sources comprise of fertilizers and pesticides, metal plating, battery industry. Toxicity of lead can be acute and chronic. The acute toxicity include headache, stomach pain, loss of appetite whereas the chronic effect is neurological damage, neurological disorder, weakness of muscle. There are numerous natural biomaterials that aid in heavy metals removal from aqueous and wastewater. Banana peel used as adsorbent for Lead removal from aqueous solution. Various agricultural wastes are use as adsorbent for heavy metal removal (Khan et al ,2004). Neem leaves has also been found as effective adsorbent for Lead removal from aqueous solution (Athar et al 2007) (Bhattacharya et al, 2004) shows that tea leaves are also efficient adsorbent in the removal of lead (II) from aqueous solution. In this paper, attempt has been done to study the carambola leaves as adsorbent for Lead removal. Various types of natural adsorbent are used for the removal of lead in the literature study. Some of them are mentioned in the table given below

Table no 1: Shows the various adsorbent used for Cd (II) ions

Adsorbent	Heavy metal	$C_{0(mg/L)}$	$q_{max(mg/g)}$	Reference
Coconut shell biochar	Pb (II)	100-2000	13.4	Paranavithana,et al , 2016)
Corncob	Pb (II)	20.7-414	16.2	Tan et al, 2010)
Lemon peel	Pb (II)	100-800	37.9	Thirumavalavanet al ,2010
Peanut shells	Pb (II)	100-350	39.0	Tasar et al, 2014
Peanut husk	Pb (II)	0-50	29.1	Qi Li et al ,2007
Sugar cane bagasse	Pb (II)	57	87.0	Abdelhafez et al , 2016
Rice husk	Pb (II)	50-200	58.0	Krishnanai et al, 2008)

The method of removal of heavy metal takes place by surface adsorption and by ion exchange method.Surface adsorption occurs by diffusion of adsorbate from aqueous solution to the surface of the adsorbent which contains opposite surface charge. The metal attaches to the surface of adsorbent by Van Der Walls forces, dipole interaction, or hydrogen binding **(**Abdelhafez et al ,2003). Ion Exchange exchange is one of the important mechanisms for metal removal**(**Eda et al ,2010)

II. Materials and Methods

2.1 Preparation of adsorbent: Wastes leaves of Averrhoa carambola were collected and washed with tap water followed by distilled water to remove dirt. It was followed by shed drying for one week and oven drying for 3 days at 105 degrees Celsius. The dried material was made into fine powder and sieved through a sieve of 75 micro mm. The powdered form was stored in air tight container inside the desiccator for future use.

Instrumentation: The characterization of the adsorbent was assessed by scanningelectron microscopy (SEM), and the presence of functional group on the adsorbent surface was done by Fourier transformance infrared spectroscopy (FTIR**)**. The surface area, pore volume is determined using BET.

Preparationof Metal Solution: Stock solution of Pb (II) is prepared by dissolving 1.6 g of Lead nitratein 1000ml of distilled water and respectiveconcentration of(5-30 mg/L)wereprepared by serialdilution ofthestock solution. The pH of the solution was adjusted using 1N NoaH and 1N HCL.

2.2 Batch Equilibrium Studies: The batch experiments were carried at room temperature in 250 ml conical flask containing 100 ml of solution. During the observation of one parameter, other parameters were kept constant. Individual batch were run for each parameter. The different parameters for removal efficiency of the adsorbent were initial metal ion concentration (5-30 mg/L), adsorbent dose (.5-4g), contact time (30-180 mins), pH(2-6). In each parameters metal ion solution and adsorbent was allowed to run in a shaker at 120 rpm.Known weightof adsorbent, Averrhoa carambola leaf (ACL) powder was measured and added to metal solution. 1 N HCL and 1 N NoaH were used to adjust the pH of metal solution. The mixture was rotated in a shaker at 120 rpm for desired setof timeintervalsAfter attaining equilibrium, the solution was filtered using Whatman Filter 41 and the filtrate was analyzed for metal concentration in AAS. A blank was taken without adsorbent. In order to avoid error experiments were conducted in triplets.

The metal removal percentage andthe amount of metal uptake were calculated as:

$\%Removal = C_i - C_f / Ci * 100$

The metal adsorption capacity of adsorbent is calculated as

$q_e = \quad C_i - C / W * V$

Where, C_i= initial metal ion concentration(mg/L), C_f= Final metal ion concentration(mg/L), qe=adsorption capacity of adsorbent(mg/g), W= mass of adsorbent(g) and V is thevolume of working solution (L).

2.3 Isotherm Models: To fit the experimental data into theoretical form, two models of isotherm were studied. Langmuir isotherm is based on the assumption of homogenous adsorption and it is expressed in linear form as:

$C_e/q_e = 1(K_L * q_m) + (C_e/q_m)$

Where, $KL_=$ Langmuir constant in mg/g,$q_{m\,=}$maximum adsorption capacity of adsorbent(mg/g)

Freundlich model: It is based on assumption of heterogeneity and adsorption takes place on heterogenous surface. It is expressed as:

$\text{Log } q_e = \text{Log } K_f + (1/n) \log C_e$

Where, K_f is adsorption capacity(mg/g), n is adsorption intensity and $\log C_e$=Equilibrium Concentration (mg/L).

2.4 Characterization of Adsorbent: Characterization of adsorbent were carried out by various methods likepH, The surface area, pore size, pore diameter was determined byBET (Brunauer–Emmett–Teller).

Statistical Analysis: Statistical analysis were done using origin software 8.5 version

III. Results and Discussion

3.1 Characterization of adsorbent

pH of the adsorbent: 10g of the adsorbent was mixed with 100ml of distilled water. The slurry was analyzed for the pH in a digital pH meter. The pH **of** the slurry was found to be 5.1. It shows that adsorbent is acidic in nature.

BET: The surface area, pore volume, pore diameter was determined using Brunauer-Emmett-Teller (BET). The surface is calculated as 96.6m2/g and pore volume are 0.05cc/g

3.2Adsorption of lead by ACL

Effect of pH on Lead adsorption: pH is important parameter in adsorption process. In the current research pH was varied from 2-6. As found by(Lee et al,1999**)** precipitation of lead occurs beyond 5. The result for the impact of change in pH shows that the optimum pH is found to be 5. The general trend for the effect of pH. shows that initially percentage removal of Pb (II) ions increases with increase in pH due to reduction in number of hydronium (H_3O+) ions. The maximum removal was at pH 5 and hence it was taken as optimum pH for rest of the adsorption process. The lowering of hydronium ions leads to easy availability of adsorbent sites by the Pb (II) ions.

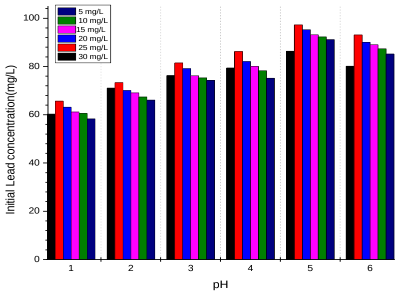


Fig 1: Effect of pH on lead adsorption by ACL

Effect of adsorbent dose: The removal percentage of Pb (II) ions with respect to dose is depicted below in Fig 2. From the given figure it is clear that the increase in dose of adsorbent increases the removal percentages but remained constant beyond 2g. The maximum removal was 96% at the dose of 2g. The removal percentage increased due to increase in adsorbent sites (Vijayaraghavanet al, 2006)greater number of adsorbent sites facilitate thePb (II) adsorption on to the adsorbent sites, further increase in dose did not increase the removal because the ratio of adsorbent to heavy metal ions increases with increase in the dose of adsorbent and large no the adsorbent sites remain unfilled. As studied by (Shukla et al, 2002**)** particle aggregation also reduces the surface area of the adsorbent and hence the removal percentage decreases.

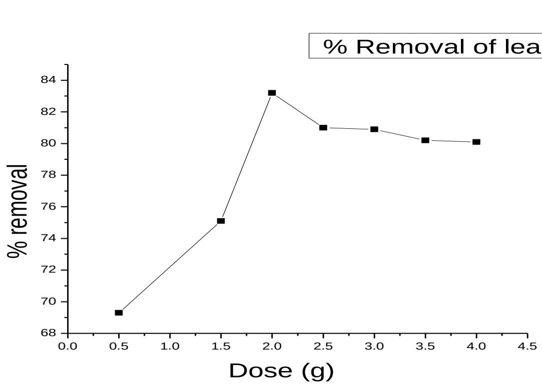
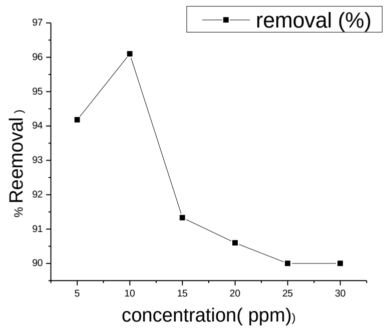


Fig 2: Effect of adsorbent dose on lead adsorption by Averrhoa carambola

Effectofinitial metal concentration: The batch experiments were carried out using different metal ion concentrationof lead (5 ,10, 15,20 ,25, 30 mg/l). Asdepicted from the figure 8, the removal of lead was highest at 10ppm (96%) and increasing the metal concentrationdoes not increasethe metal removal percentage because of saturation of binding sites of adsorbent. At lowerconcentration of metal ions adsorbent has more binding sites but as the concentration increases, these binding sitesgetfilled up andtherestofthe metalionsremainsinthesolution withoutadsorption.



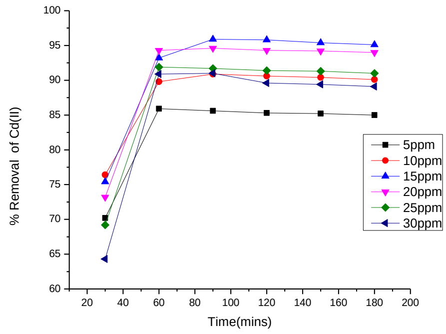


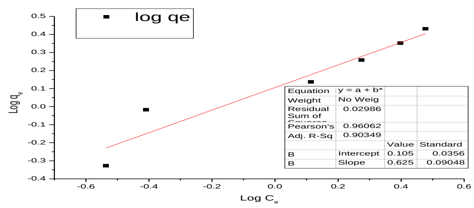
Fig 3: Effect of initialmetal concentration on lead adsorption ACL

Fig 4: Effect of contact time on lead adsorption by ACL

Effect of contact time: The effect of contact time between adsorbate and adsorbent is given below. The results shows that the metal adsorption takes place in important stages. a) initial phase b) rapid phase c) equilibrium phase. During initial phase, large number of adsorbent sites are available for the Pb (II) ions to form bond with the adsorbent. In rapid phase, the interaction of Pb (II) ions with the pores of adsorbent sites and the chelation of Pb (II) ions and the functional group of the adsorbent takes place. At equilibrium phase, no further increase in removal percentage takes place. Here, equilibrium was attained at 60 mins. Therefore, 60 mins was taken as optimal contact time for rest of the adsorption process.

Isothermal models: To determine the isotherm model, experiment was conducted at optimal values i.e., pH 5, concentration of 10 mg/L, contact time of 60 mins and at the dose of 2g.

a



b

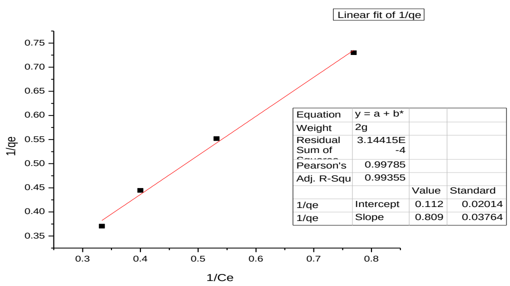


Fig 5: a. Langmuir isotherm for adsorption of lead by ACL b. Freundlich isotherm for adsorption of lead by ACL

From the above figure it is clear that the regression coefficient (R^2 =.9935) value for Langmuir is higher than the (R^2=.903) value for Freundlich. Hence, Pb (II) ions fits best to Langmuir model. This suggest that the adsorption takes place on monolayer surface. The maximum metal adsorption capacity was found to be 8.45 mg/g. The type of the adsorption isotherm is determined by separation factor R_L.It is unfavorable (R_L>1), linear (R_L=1) and irreversible (R_L=0). In the present work, value of RL is found to be .411 which falls in the region of 0-1. This concludes that the adsorption process is favorable in nature. Moreover, the Freundlich constant n(1.275) is also in the region of 0-10 which suggest favorable adsorption

Metal	Langmuir isotherm	Freundlich isotherm
Pb (II) ions	q_{max} =8.45mg/g	N=1.275
	K_L (L/mg) = .1388 R_L =.411	K_f (mg/g) = 1.2
	R^2 =.9935	R^2 =.903
	Slope=0.809	Slope=1.47503
	Intercept =0.112	Intercept =0.292

Table 2. Langmuir and Freundlich Parameters

The adsorption of lead onto the surface of the adsorbent could be due to more electronegativity of the Pb (II) ions. As studied by [adsorption of some metal ions is due to property of electronegativity, ionic radii and paramagnetic nature.

IV. Conclusions

The research finding proves that Averrhoa carambola leaves (ACL) proves to be efficient adsorbent for the removal of Pb (II) ions from synthetic water. The factors such as initial metal ions, adsorbent dose, pH, contact time effect the adsorption process. Increase in initial lead concentration decreases the adsorption process by ACL.The optimum parameters for equilibrium adsorption was found to be 10 mg/L, dose of 2g and solution pH of 5 at 60mins of contact time.The equilibrium model reveals that Langmuir isotherm model gave best fit for Pb (II) with R^2value .9935.

Declaration of competing interest

The author declares no conflict of interest

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References

[1]. Abdelhafez, A. A., & Li, J. (2016). Removal of Pb (II) from aqueous solution by using biochar derived from sugar cane bagasse and orange peel. *Journal of the Taiwan Institute of Chemical Engineers*, *61*, 367-375.

[2]. Ahalya, N., Ramachandra, T. V., &Kanamadi, R. D. (2003). Biosorption of heavy metals. *Res. J. Chem. Environ*, *7*(4), 71-79.

[3]. Athar, M., Farooq, U., & Hussain, B. (2007). Azadirachata indicum (neem): an effective biosorbent for the removal of lead (II) from aqueous solutions. *Bulletin of environmental contamination and toxicology*, *79*(3), 288-292.

[4]. Bhattacharyya, K. G., & Sharma, A. (2004). Adsorption of Pb (II) from aqueous solution by Azadirachta indica (Neem) leaf powder. *Journal of hazardous materials*, *113*(1-3), 97-109.

[5]. Charerntanyarak, L. (1999). Heavy metals removal by chemical coagulation and precipitation. *Water Science and Technology*, *39*(10-11), 135-138.

[6]. Eda, G., Lin, Y. Y., Mattevi, C., Yamaguchi, H., Chen, H. A., Chen, I. S., ... &Chhowalla, M. (2010). Blue photoluminescence from chemically derived graphene oxide. *Advanced materials*, *22*(4), 505-509.

[7]. Fergusson, J. E. (1990). The heavy elements: Chemistry, environmental impact and health effects. *PERGAMON PRESS, OXFORD(UK). 1990. (II)fromaqueoussolution*,Bull.Environ.Contam.Toxicol 79(2007)288-292

[8]. Huang, J., Li, Q., Sun, D., Lu, Y., Su, Y., Yang, X., ... & Chen, C. (2007). Biosynthesis of silver and gold nanoparticles by novel sundried Cinnamomum camphora leaf. *Nanotechnology*, *18*(10), 105104.

[9]. Khan, N. A., Ibrahim, S., & Subramaniam, P. (2004). Elimination of heavy metals from wastewater using agricultural wastes as adsorbents. *Malaysian journal of science*, *23*(1), 43-51.

[10]. Krishnani, K. K., Meng, X., Christodoulatos, C., &Boddu, V. M. (2008). Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk. *Journal of hazardous materials*, *153*(3), 1222-1234.

[11]. Manjuladevi, M., Anitha, R., &Manonmani, S. (2018). Kinetic study on adsorption of Cr (VI), Ni (II), Cd (II) and Pb (II) ions from aqueous solutions using activated carbon prepared from Cucumis melo peel. *Applied water science*, *8*(1), 1-8.'

[12]. Nagajyoti, P. C., Lee, K. D., & Sreekanth, T. V. M. (2010). Heavy metals, occurrence and toxicity for plants: a

review. *Environmental chemistry letters*, *8*(3), 199-216.

[13]. Nandiyanto, A. B. D., Oktiani, R., &Ragadhita, R. (2019). How to read and interpret FTIR spectroscope of organic material. *Indonesian Journal of Science and Technology*, *4*(1), 97-118.

[14]. Paranavithana, G. N., Kawamoto, K., Inoue, Y., Saito, T., Vithanage, M., Kalpage, C. S., & Herath, G. B. B. (2016). Adsorption of Cd2+ and Pb2+ onto coconut shell biochar and biochar-mixed soil. *Environmental Earth Sciences*, *75*(6), 1-12.

[15]. Šćiban, M., Radetić, B., Kevrešan, Ž., &Klašnja, M. (2007). Adsorption of heavy metals from electroplating wastewater by wood sawdust. *Bioresource technology*, *98*(2), 402-409.

[16]. Sulyman, M., Namiesnik, J., &Gierak, A. (2017). Low-cost Adsorbents Derived from Agricultural By-products/Wastes for Enhancing Contaminant Uptakes from Wastewater: A Review. *Polish Journal of Environmental Studies*, *26*(3).

[17]. Taşar, Ş., Kaya, F., &Özer, A. (2014). Biosorption of lead (II) ions from aqueous solution by peanut shells: equilibrium, thermodynamic and kinetic studies. *Journal of Environmental Chemical Engineering*, *2*(2), 1018-1026.

[18]. Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., & Sutton, D. J. (2012). Heavy metal toxicity and the environment. *Molecular, clinical and environmental toxicology*, 133-164.

[19]. Thirumavalavan, M., Lai, Y. L., Lin, L. C., & Lee, J. F. (2010). Cellulose-based native and surface modified fruit peels for the adsorption of heavy metal ions from aqueous solution: Langmuir adsorption isotherms. *Journal of Chemical & Engineering Data*, *55*(3), 1186-1192.

[20]. Vijayaraghavan, K., Padmesh, T. V. N., Palanivelu, K., &Velan, M. (2006). Biosorption of nickel (II) ions onto Sargassum wightii: application of two-parameter and three-parameter isotherm models. *Journal of hazardous materials*, *133*(1-3), 304-308.

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