Est. 1984

ORIENTAL JOURNAL OF CHEMISTRY

An International Open Access, Peer Reviewed Research Journal

www.orientjchem.org

ISSN: 0970-020 X
CODEN: OJCHEG
2022, Vol. 38, No.(4):
Pg. 906-913

Screening of Newspaper Pulp as a Potential Adsorbent for Impounding Pb^{2+} Ions from Aqueous Hinterlands

N. SHYAMALA DEVI[1]* and C. SWATHI SRI[2]

[1,2]Department of Chemistry, PSGR Krishnammal College for Women, Peelamedu, Coimbatore, Tamil Nadu, India.
*Corresponding author E-mail: shyamalapsgr@gmail.com

http://dx.doi.org/10.13005/ojc/380410

(Received: May 27, 2022; Accepted: July 12, 2022)

ABSTRACT

Intensification of industrial activity, environment stress contributes to the significant rise of heavy metal pollution in water resources. Pollution due to malignant heavy metals such as lead, chromium, arsenic etc., has been tremendously focused on communal health. Lead pollution-potable water finds great threat by different sources like plating units, lead pipes etc., Newspaper is a cellulosic materials, containing cellulose, hemicellulose and other inorganic fillers. The present study evaluates the potentiality of modified newspaper pulp for sequestration of Pb(II) ions. Characterizations of loaded and unloaded pulp were evaluated by FTIR, SEM and EDAX assay. Batch experimental studies were accomplished to assess the equilibration between the sorbate-sorbent through various operating factors viz., pH, dosage, time course, initial concentration, influence of ions, co-ions and effect of temperature. The residual concentrations of the Pb^{2+} ions from aqueous solutions are examined by UV-Visible Spectrophotometer. The equilibrium data was appropriately fitted with Langmuir adsorption isotherm model.

Keywords: Newspaper Pulp, Lead, Batch Studies, Isotherms.

INTRODUCTION

In accordance with environment, water is the most essential source for well-being of living organisms. As a result of distinct effects on the water resources, especially contaminants through human activities such as heavy metals, sewage discharges, disease causing agent, organic and inorganic pollutants, water is being polluted and still it is used unconsciously. The major sources of heavy metals from electroplating industries, tanneries, mining, textile, battery[1]. Wide methods of treatment have been employed for curbing of heavy metals from waste water. The methods include coagulation, chemical precipitation, filtration, membrane separation, adsorption, ion exchange. Above all the techniques, adsorption is a promising and possible technique for heavy metal removal comprising high efficiency with a low cost approach[2]. The current study is aimed at the assessment screening of a low cost biomaterial for a potential sorption towards heavy metal ions. Large number of low cost eco-materials viz., sawdust, coconut husk, rice husk etc.,[3,4] Newspaper pulp, a source of cellulose, is chosen as an adsorbent material. The utilization of newspaper pulp for curbing Pb(II) ions from wastewater is considered to be an exclusive study.

Lead is a malignant pollutant in air and in drinking water. The presence of high quantity of lead in plants produces reactive oxygen species, causing lipid membrane damage suppressing the overall growth of the plant. The Permissible standard of lead in potable water is about 0.010 mg/L according to BIS and WHO standards[5] . Contamination of lead in drinking water endures adverse ill effects viz., skin irritation, nausea, lung cancer etc.,

To march ahead the above crisis the research survey had aimed to emphasize the chemically modified newspaper pulp as an alternative potential low cost adsorbent for sequestration of Pb(II) ions from aqueous matrices[6]. Batch studies were accomplished to measure the influence of pH, sorbent dosage, time course, initial concentration, influence of ions, co-ions impact, effect of temperature and desorption studies.

EXPERIMENTAL METHODS

Pre-Modification of Newspaper Pulp (PMNPP)

Newspaper was collected from home, offices and waste paper mart in Coimbatore, Tamil Nadu, India. The collected materials were cut into small bits. 50 g of newspaper bits was weighed and liquefied with $NaHCO_3$ solution with continuous stirring until the formation of pulpy nature (Fig. 1a). Then, the pulp was filtered and washed with doubly distilled water until pH attains 6.5-7.0. After filtration, a homogenized pulp was obtained and dried in oven. The dried pulp was pulverized using mixture grinder to impart a fibrous consistency and larger surface area than the raw newspaper.

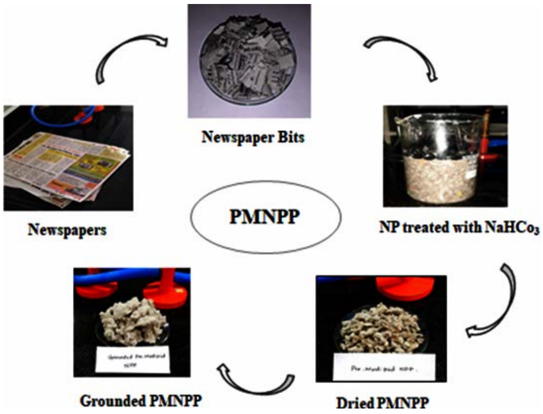

Fig. 1(a). Pre-Modification of NPP

Chemical Modification of Newspaper Pulp

The pre-modified newspaper pulp (PMNPP) was chemically modified using 0.1 N Citric Acid (CA), the pulp was completely immersed in the acid solution (Fig. 1b). The modification was based on the addition of C=O from citric acid to the pre-modified pulp. Then, the addition of acidic anhydride between the C=O group by the removal of water leads to ester linkage between the OH molecule of cellulose and anhydride. The mixture of CA and NPP were agitated at 120 rpm for 90 min in Kemi Oribtal mechanical shaker. After agitation, the mixture was then washed with water to remove the excess acidic nature. The Citric Acid Modified Newspaper Pulp (CAMNPP) was dried and pulverized to procure the same consistency as the PMNPP. Only the modified Newspaper Pulp sorbent material (CAMNPP) was employed for further experiments.

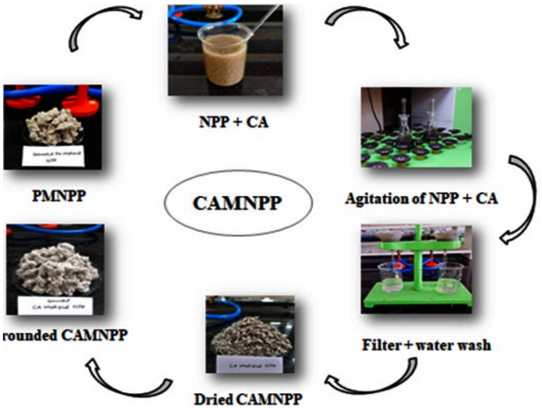

Fig. 1(b). Chemical-Modification of NPP

Preparation of Stock solution

A stock solution of 1000 mg/L of Pb(II) was prepared by dissolving 1.5985 g of Lead Nitrate $[Pb(No_3)_2]$ in doubly distilled water. Standard solution of 500 mg/L, 250 mg/L and 100 mg/L was prepared from the stock solution for further studies.

Pilot Study-Batch Equilibration Technique

The sorption experiments were accomplished in a batch process at room temperature. 0.25 g, 0.50 g, 0.75 g and 1.0 g of the sorbent (CAMNPP) was added to 50 mL of adsorbate with an initial concentration of 100 mg/L, 250 mg/L, 500 mg/L and 1000 mg/L of Pb(II) aqueous solution. The solutions were agitated in Kemi Orbital mechanical shaker at 120 rpm for a definite period of 5 min time interval. Sorption parameters such as adsorbent dosage, time course and pH were enhanced by the process of continuous variation. The contents were then filtered and Pb(II) concentration was measured before and after adsorption (Residual concentration) using UV-Visible Spectrophotometer (LABINDIA) instrument.

RESULT AND DISCUSSION

Adsorption Studies Using CAMNPP

The CAMNPP of dosages 0.25 g, 0.50 g, 0.75 g and 1.0 g were employed as the adsorbent in the sorption studies of Pb(II) ions. The discussions of the experimental results are presented below.

Batch Equilibrium Studies

Adsorbent dosage onto sorption

The active sites availability for the uptake of sorbate ions depends on the addition of varying doses of sorbents. The influence of dosage disparity (viz., 0.25 g, 0.50 g, 0.75 g & 1.0 g) for the Pb(II)- CAMNPP experimented system is depicted in Fig. 2. A steep inclination was observed in the curve of CAMNPP up to 100 mg/L beyond which a saturation point is reached at higher concentrations, where maximized curve is seen for 1.0 g dose[8]. The dosage of the adsorbent material determined has accounted for the maximum removal of sorbate, this was taken as the optimum condition for further sorption studies.

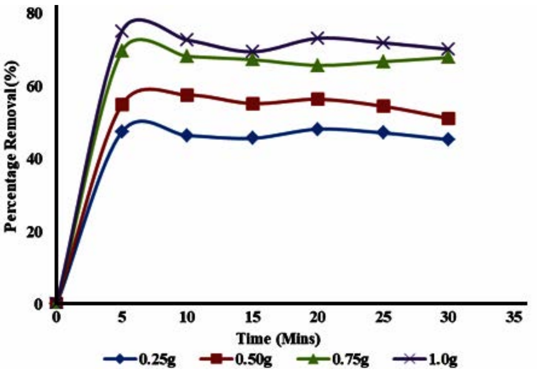

Fig. 2. Effect of adsorbent dosage

Initial Concentration and Time Course onto sorption

The impact of Pb(II) initial concentration and time course schemes at present conditions for CAMNPP was depicted in Fig. 3. It reveals consistent increments in the amounts of Pb(II) adsorbed for 100 mg/L by the display of smooth plateau. Attainment of an stability state is emphasized at 100 mg/L Pb(II) concentration at 5 min time course. It suggests the possibility of monolayer coverage upon CAMNPP. Also, reduced amounts of Pb(II) adsorbed at concentration higher than 100 mg/L imply the availability of limited sorption sites ratio between sorbent-sorbate species[9]. Henceforth, a minimum period of 5 min and 100 mg/L initial concentration have been chosen as the optimized conditions for Pb(II)-CAMNPP system. The deduction efficacy of Pb(II) by CAMNPP enlarged due to the lavish accessibility of active sites on the sorbent material.

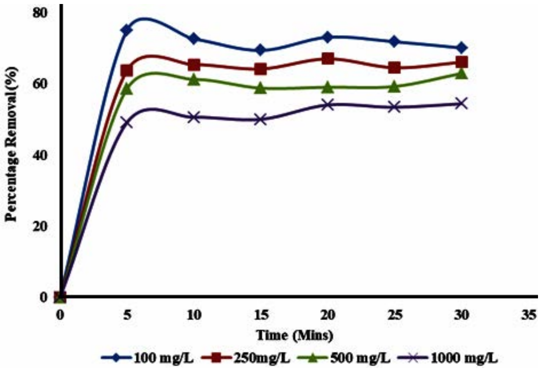

Fig. 3. Initial Concentration & Time course onto sorption

pH onto sorption

Approximate parabolic curves for the impact of pH onto Pb(II)-CAMNPP system is depicted in Fig. 4. Maximum percentage removal (75%) had occurred at pH 5.0 followed by a dip in the curve. This is supported by the findings of N. M. Andal *et al.,*[1] where less sorption at acidic pH show that H^+ ions compete to get adsorbed ahead of Pb^{2+} ions. Similarly, diminished sorption at alkaline pH support the complex formation of Pb^{2+} ions with hydroxyl ions.

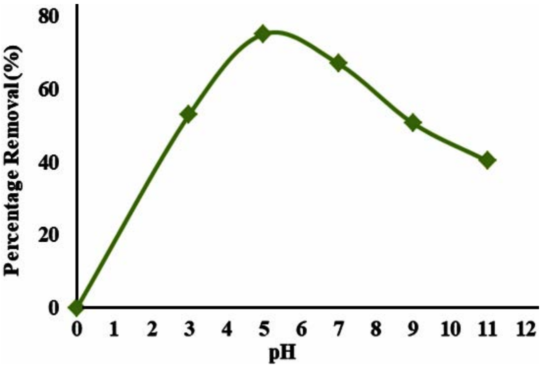

Fig.4. Effect of pH

Effect of Cations

The influence of sodium and potassium

ions on the Pb(II)-CAMNPP system from the resulting adsorption experiments is shown in Fig. 5. The reduction in the deduction of Pb^{2+} ions at different K^+ ion environment implies a gradual decrease in the rate of Pb^{2+} ions getting adsorbed over the surface of the CAMNPP, as compared to that of Na^+ ion environment matrices. The effect of K^+ ion in reducing the adsorption of lead(II) ion is greater when compared to that of Na^+ ion. This is because smaller the size of an ion, greater the degree of its hydration, as supported with D. Harikishore Kumar Reddy *et al.,*[10] As Na^+ ion is smaller in size its hydration is more effective and its inhibition for the Pb(II) uptake by CAMNPP is less in comparison with K^+ ion interference.

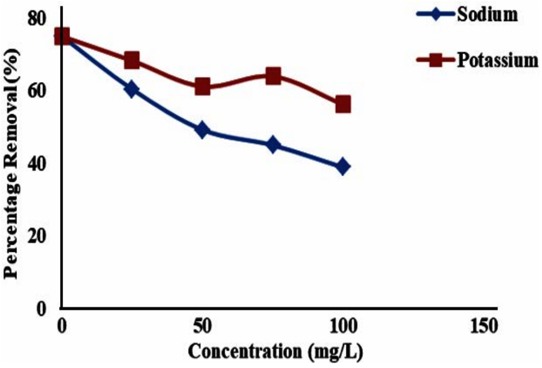

Fig.5. Effect of Cations

Effect of Anions

The sorption studies were accomplished in the presence of two different anions Viz., Carbonate (CO_3^{2-}) and Sulphate (SO_4^{2-}) along with Pb(II) ions in different concentrations and the results were potted in Fig. 6. The outcomes instance that the adsorption capacity of Pb(II)-CAMNPP system was reduced with escalation in concentration of anions. The presence of CO_3^{2-} and SO_4^{2-} anions influenced the ability of Pb(II) ions in surface matrices. Hence, desired anions have a durable obstruct effect and CAMNPP material has more attraction towards highly charged anions.

Effect of Co-ions

The result of the analysis at the influence of Co-ions (Viz., Zinc and Nickel) reveals that the presence of the foreign ions diminished the sorption rate (Fig. 7). The effects of Co-ions of varying concentrations ranging from 0-100 mg/L shows, it is obvious that the percentage of Pb(II) removed by CAMNPP (75%) in the absence of other ions was found to reduce nearly 69.43% in the presence of Zn(II). The presence of Ni(II) as a Co-ion reduced the presence of Pb(II) to 70.51%.

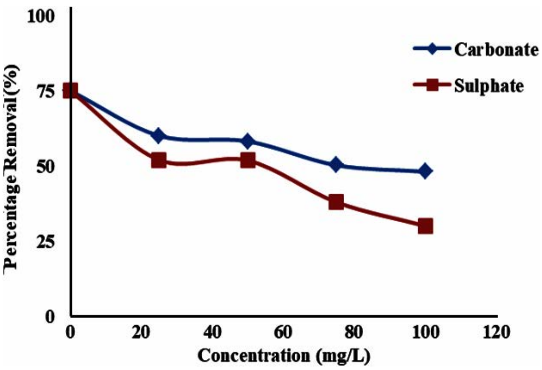

Fig.6. Effect of Anion

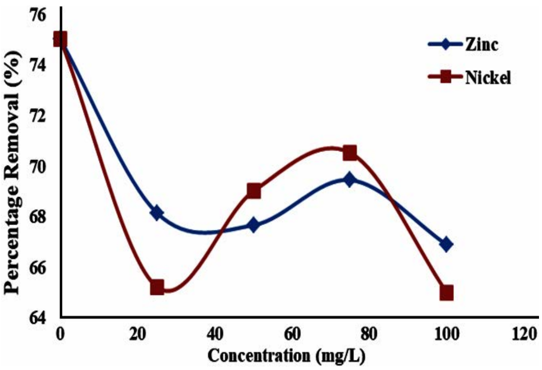

Fig.7. Effect of Co-ions

Temperature onto sorption

The temperature (293-323 K) on Pb(II) sorption using CAMNPP (Fig. 8) initiated a shoot up in the Pb(II) removal at 303K, beyond which an increment was observed at higher temperatures due to flexibility of adsorbate species aiding to a sorption improvisation. The rise in numerous active sites availability for sorption process leads to the swelling of sorbent material, so that there might be a decline in the boundary layer thickness on all the sides of the chosen material. Similar results have been observed by Nisha Gaur *et al.,*[11] which shows the mobility of metal ions increases at higher temperature.

Desorption of Pb(II)

Desorption studies probes the possibility of reprocessing the loaded adsorbents and regenerating the same for further sorption process. Studies were carried out for Pb(II)-CAMNPP systems to assess the efficiencies of the packed sorbents by employing various strengths of HCl. Fig. 9 indicates that the percentage of desorption was inversely proportional to the concentration of HCL vicinity.

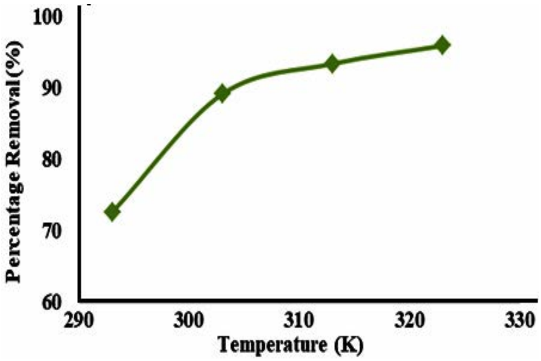

Fig. 8. Effect of Temperature

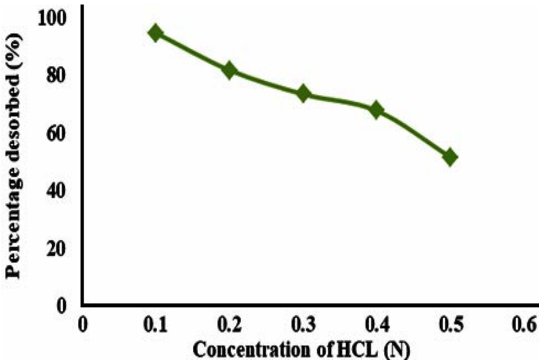

Fig. 9. Desorption of Pb(II)

Material Screening
FTIR Spectroscopic Analysis (SHIMADZU)

The FTIR spectra of CAMNPP and Pb(II) loaded NPP lies between 4000-400 cm^{-1} characteristic region providing cellulose peaks at 1056.99 cm^{-1} and 1026.13 cm^{-1}. The spectral bands 1103.28 cm^{-1} and 1157.29 cm^{-1} also corresponds to cellulose (Mardiah *et al.,*[14]). In FTIR spectra of CAMNPP (Fig. 10), the band at 1689.64 cm^{-1} resembles the active vibrations of fibrous sorbent material due to the absorption of water molecule. The spectral band 1743.65 cm^{-1} indicates the ester linkage between NPP and Citric acid. In FTIR spectra of Pb(II) loaded NPP (Fig. 11) , the extent of band shifting in the region of 1026.13 cm^{-1} indicates the point of interface between functional groups and Pb^{2+} ions. After adsorption, the intensity of peaks becomes reduced and stipulated the involvement of metals over the surface of the sorbent material.

SEM Micrograph Analysis (JEOL)

The morphology of Raw NPP portrayed in the Fig. 12, discloses the presence of irregular fibers, which are arranged randomly in horizontal and vertical directions with plenty of adhesives and ink. The microstructure of PMNPP (Fig. 13) consists of fine pores which are filled by agglomerated fibers and alkali metal ions. The surface of CAMNPP (Fig. 14) consists of less flocs with more consistent than PMNPP. After CA modification, the alkali's presents on the fibrous materials are diminished. The pores are opened for the entry of contaminant particles and thus CAMNPP helped in sorption process. After sorption process, the metal Pb(II) deposited on the fibrous surface of CAMNPP exposed in SEM image (Fig. 15). Interaction with Pb(II) indicates the presence of patches over the surface through Vander Waal's force (Physisorption).

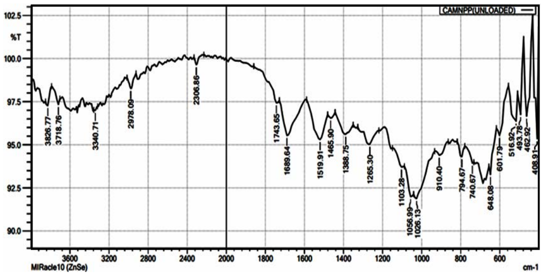

Fig. 10. FTIR-CAMNPP

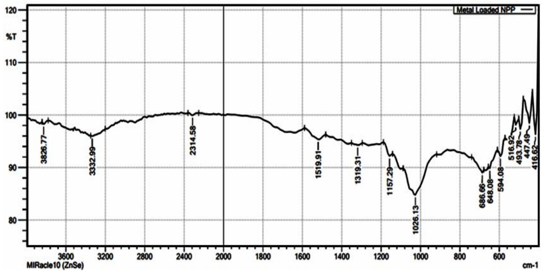

Fig. 11. FTIR - Pb(II) loaded CAMNPP

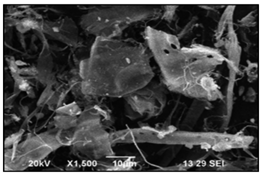

Fig. 12. Raw NPP

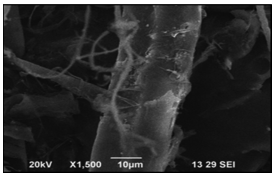

Fig. 13 PMNPP

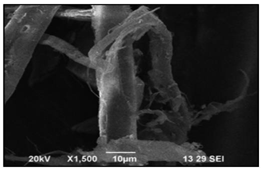

Fig. 14. CAMNPP

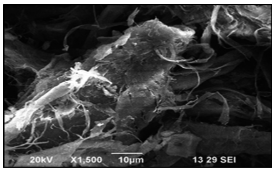

Fig. 15. Pb(II) loaded CAMNPP

EDAX Spectrum Elemental Analysis (JEOL)

The EDAX spectrum depicted in Fig. 16 of raw NPP reveal the existence of the main elements such as Ca, O and Si whereas, the material PMNPP Fig. 17 in contains C, O and inorganic salts such as Ca, K, Si, Al. Similarly, the material CAMNPP (Fig. 18) contains C, O, Ca, Si and Al. The spectrum of Pb loaded NPP (Fig. 19) consists of O, Ca, Al and Si. Cellulose, a main component of newspaper is primarily composed of C and O. The others elements such as inorganic salts exist from stuffs the added by paper mills.

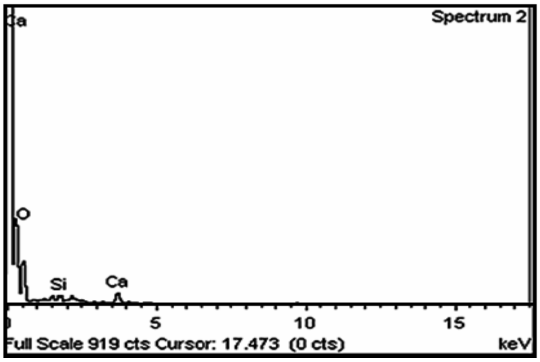

Fig. 16. EDAX spectrum of Raw NPP

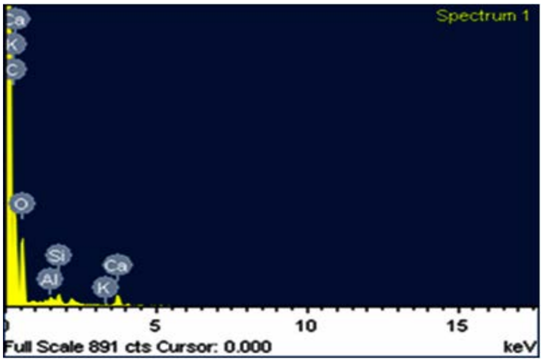

Fig. 17. EDAX spectrum of PMNPP

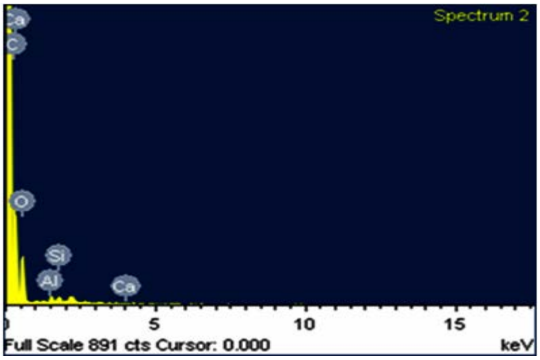

Fig. 18. EDAX spectrum of CAMNPP

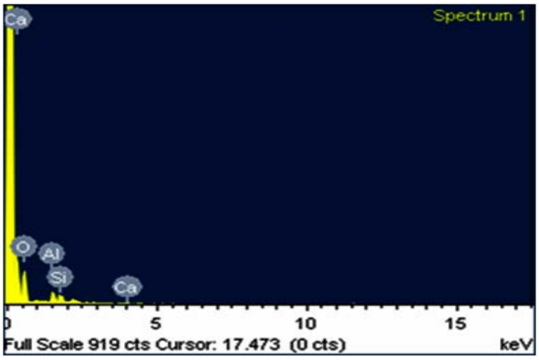

Fig. 19. EDAX spectrum of Pb(II) loaded CAMNPP

Adsorption Isothermal Studies

Adsorption isotherm is a key domain to determine the adsorption process. Different adsorption isotherm models viz., Langmuir, Freundlich and Temkin have been deliberated for the verified system.

Langmuir Model

The Langmuir plot of Ce/qe vs Ce is described in Fig. 20. The Langmuir constants q_m and n are obtained from the the plot (Table 1) From the correlation coefficient (R^2) value (0.999), it is evident that Langmuir adsorption model fitted with the adsorption of Pb(II)-CAMNPP sorbent system. A uniform adsorption occurs between Pb^{2+} ions and CAMNPP onto single molecular layer scheme. In accordance, all the RL values presented in Table 2 are less than zero. Hence, the deduction of lead is favourable at different desired concentrations.

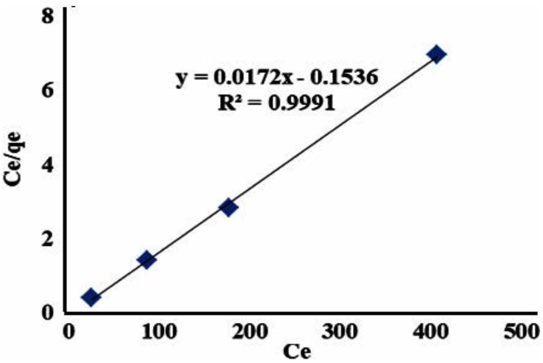

Fig. 20. Langmuir Plot

Freundlich Model

The Freundlich constants K_f and n are attained from the the plot log qe vs log Ce as (Fig. 21). The obtained 1/n value indicate the interface between the CAMNPP and Pb(II). The factors of the Freundlich isotherm (Table 1) indicate that the model has fitted well according to the correlation coefficient (R^2). Even though 1/n values are less than unity, lower R^2 values are obvious than Langmuir. Hence, Freundlich model is less favored by the system.

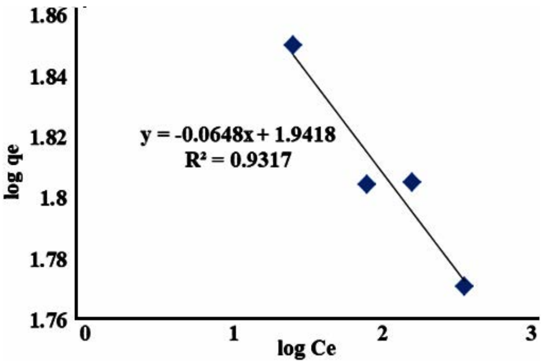

Fig. 21. Freundlich Plot

Temkin Model

The plot of qe vs ln Ce representing the Temkin model was shown in Fig. 22. The factors and the corresponding R^2 value, were listed in Table 1. It is found that the Temkin adsorption model fitted with Pb(II)–CAMNPP system which shows a uniform distribution of adsorbate onto adsorbent surface. The R^2 value is small compared to Langmuir and Feundlich adsorption isotherms.

Evaluation of R^2 Factor

The correlation coefficient (R^2) of all the three isotherms Viz., Langmuir (0.9991), Freundlich (0.9317) and Temkin (0.9297) are fitted well with Pb(II)–CAMNPP system. According to R^2 value, the order of adsorption isotherm models obtained as Langmuir > Freundlich > Tempkin. Similary, the sorption study of M. K. Monda *et al.,*[17] utilizing activated tea waste. It is evident that the Langmuir model describes the best sorption coverage onto Pb(II)–CAMNPP system.

Adsorption Dynamics

ΔH^0 and ΔS^0 calculated from Van't Hoff 's plots (Fig. 23) are presented in Table 3. Nature of feasibility, spontaneity and exothermicity are arrived from the negative values of ΔG^0 and ΔH^0. Positive ΔS^0 values show the intensification of randomness at the sorption interface. Similar trends were also observed by S. Tasar *et al.,*[20]

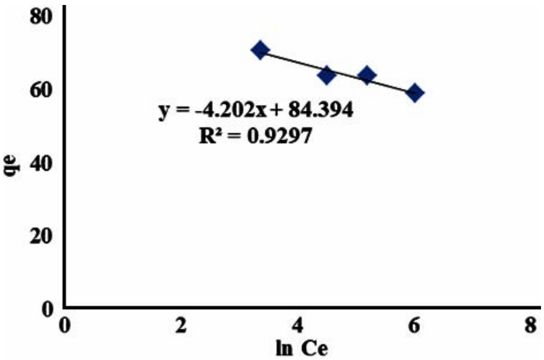

Fig. 22. Temkin Plot

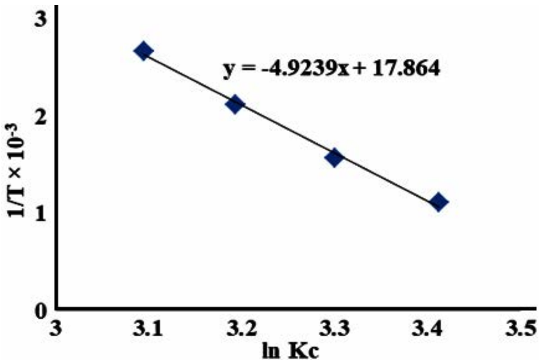

Fig. 23. Van't Hoff's Plot

Table 1: Isothermal Constants

System	Langmuir			Freundlich			Temkin		
	q_m (mg/g)	b (L/g)	R^2	K_F (mg/g)	1/n	R^2	AT(Lg^{-1})	B (Jmol^{-1})	R^2
Pb(II) – CAMNPP	58.13	1.33	0.999	87.45	-0.0648	0.9317	0.864	-4.202	0.929

Table 2: Equilibrium parameter (RL)

Desired Concentrations (mg/L)	Pb(II)-CAMNPP
100	0.077
250	0.034
500	0.017
1000	0.008

Table 3: Thermodynamic Parameters

Temp.(K)	Pb(II)-CAMNPP		
	$\Delta G°X10^{-3}$(kJ/mol)	$\Delta H°$(kJ/mol)	$\Delta S°$(J/mol K)
293	-0.268	- 4.923	17.86
303	-0.394		
313	-0.549		
323	-0.714		

CONCLUSION

Citric Acid Modified Newspaper Pulp (CAMNPP) was utilized as a sorbent to sequestrate Pb^{2+} ions from aqueous environs. The characterization of adsorbents was evaluated by FTIR, SEM and EDAX assay. The studies indicate that a maximum of Pb(II) adsorption capacity was achieved by 75% sequestration with an adsorbent dosage of 1.0 g and time course of 5 min at optimum pH 5.0 with an initial concentration of 100mg/L. The adsorption of the metal ion was significantly influenced by the presence of cations, anions, and co-ions. The Langmuir model fitted well with adsorption equilibrium data. The nature of feasibility, spontaneity and exothermicity was confirmed by adsorption dynamic data. It is evident that CAMNPP was found to be suitable and effective adsorbent with higher chelating ability in the removal of Pb(II) ions.

ACKNOWLEDGMENT

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Conflict of interest

The author declare that we have no conflict of interest.

REFERENCE

1. Shyamala Devi, N; Muthulakshmi Andal, N; Vivithabharathi, K; *Orient. J. Chem.*, **2018**, *34*, 352-361.
2. Chakraborty, R; Asthana, A; Singh, A.K; Jain, B; Hasan Susan, A.B; *Int. J. Environ. Anal. Chem.*, **2020**, *102*, 342-379.
3. Hegazi, H.A; *HBRC Journal.*, **2013**, *9*, 276-282.
4. Alli Shaikh, T.M; *Biointerface Res. Appl. Chem.*, **2020**, *10*, 6522-6539.
5. Kaushal, A; Singh, A.K; *Int J Hydro.*, **2017**, *1*(2), 1-11.
6. Moyib, O. K.; Ayedun , M. A.; Awokoya, O. J.; Omotola, O. E, *Niger. J. Chem. Res.*, **2017**, *22*, 29-39.
7. Rahaman, Md. H.; Islam, Md. A.; Islam Md. M.; Rahman, Md. A.; Nur Alam S.M.; *Curr. Res. Green. Sustain. Chem.*, **2021**, *4*, 1-8.
8. Bagali, S.S.; Gowrishankar, B.S.; Roy, A.S.; *Engineering.*, **2017**, *3*, 409–415.
9. Sai Seetha Rama Raju, D.; Nageswara Rao, V.; Rajendra Prasad, P.; Chitti Babu, N.; *Int. J. Eng. Sci. Technol.*, **2012**, *2*, 1577–1581.
10. Harikishore Kumar Reddy, D.; Seshaiah, K.; Reddy, A. V. R.; Madhava Rao, M.; Wang, M.C; *Mater, J.H.*, **2010**, *174*, 831-838.
11. Gaur, N.; Kukreja, A.; Yadav, M.; Tiwari, A.; *Appl. Water Sci.,* **2018**, *4*(4), 75-81.
12. Khalifaa, R. E.; Abd-Eldayemb, S. N.; Abd-Elmageedb, M. H.; Tamera, T. M.; Omera, A. M.; Mohy Eldin, M. S.; *Desalination Water Treat.*, **2021**, *229*, 167-183.
13. Chen, H.; Meng, Y.; Jia, S.; Hua, W.; Cheng, Y.; Lu, J.; Wang, H.; *J. Pre-proof.*, **2020**.
14. Mardiah.; Fathoni, R.; Pudyaningtyas, P.; Gamu, H.; Rinaldy.; *MATEC Web of Conferences.*, **2018**, *156*, 1-5.
15. Mishr., *Biointerface Res. Appl. Chem.*, **2022**, *12*, 1884–1898.
16. Ghorbani,M.; Seyedin, O.; Agha mohammad hassan, M., *J. Environ. Manage.*, **2020**, *254*, 1-15.
17. Monda, M. K., *Korean J. Chem. Eng.*, **2010**, *27*(1), 144-151.
18. Varghese, A.G.; Paul, S. A.; Latha, M.S.; *Environ. Chem. Lett.*, **2019**, *17*, 867–877.
19. Abdelhamid, H. N.; Mathew, A.P.; *Front. Chem. Eng.*, **2021**, *3*, 1-23.
20. Tasar, S.; Kaya, F.; Ozer, A.; *J. Environ. Chem. Eng.*, **2014**, *2*, 1018-1026.