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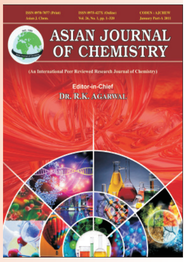

Adsorptive Removal of Pb(II) from Water Using Novel Synthesized Polyaniline Composites with *Madhuca longifolia* and *Eugenia jambolana* Leaf Powder

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Novel polyaniline composites with plant leaf powder of *Madhuca longifolia* (Mahwa) and *Eugenia jambolana* (Jamun) (PANI/ML, PANI/JL) were synthesized for removal of Pb(II) from water. The optimum conditions of sorption were found on batch scale as followed: adsorbent dose 0.8 g in 50 mL solution of Pb(II), 90 min contact time, 4 pH and 30 °C temperature for PANI/ML and for PANI/JL: adsorbent dose 0.9 g in 50 mL solution of Pb(II), 90 min contact time, 2 pH and 50 °C temperature. Langmuir and Freundlich isotherm models were subjected to sorption data. Langmuir isotherm indicated monolayer chemisorptive removal of lead ions occurred more on homogeneously distributed binding sites on composites. The negative value of $\Delta G°$ confirmed the spontaneity and feasibility of adsorption process with maximum removal of Pb(II), whereas Freundlich model applicability indicated that binding sites are heterogeneously distributed in composites, facilitates physiosorptive removal of metal ions. K_F values were: 0.857 and 0.500 for PANI/ML and PANI/JL respectively. The maximum adsorption capacities of PANI/ML composites is 3.891 mg/g, while in case of PANI/JL it was 5.917 mg/g. Results indicated that for Pb(II) removal, PANI/JL is better adsorbent and shows more adsorption as compared to PANI/ML.

Keywords: Adsorption, Lead, Polyaniline, composites, *Madhuca longifolia*, *Eugenia jambolana*.

INTRODUCTION

Water is very important for life on earth. Heavy metals are unpleasant, affecting our ecosystem due to their toxic and physiological effects on environment[1]. Main heavy metals are Cd(II), Pb(II), Cr(VI), Hg(II), Cu(II) and Ni(II). Among them, lead is very toxic even in very low concentration in water[2]. Most elusive environmental health threat is the lead contamination as lead exposure is linked with death and disease in animals humans and birds. Most important sources of pollution by lead are: battery manufactures, automobiles, radioactivity shields, plumbing fixtures, cable coverings, ammunition, paint pigments, caulking, solder, printed circuit boards, bearings, textile industries, petroleum industries and electroplating[3,4]. Rivers and streams are contaminated with its elevated levels. Leaching from soil is the natural cause of this metal contamination, but it is augmented due to above mentioned sources *i.e.* industrial waste water runoff or mine tailing[5].

Concentrations of Pb(II) ions are about the range of 200-500 ppm in industrial waste water. According to water quality standards it is very high and it must be reduced to value of 0.10-0.50 ppm[6]. Main target of lead in an organism body is CNS, kidney, liver and reproductive system. Its toxic symptoms are insomnia, anemia, dizziness, headache, irritability, weakness of muscles, renal damages and hallucination[7]. For removal of heavy metals, methods used are: reverse osmosis, chemical precipitation, ion exchange, electrolytic process, solvent extraction and adsorption[8]. Amongst them, reverse osmosis is though very efficient but is a costly and too expensive process as membranes get easily blemished and required regular replacement. Chemical precipitation is not very suitable when pollutants are present in less amounts. Ion exchange is luxurious while electrolytic process or solvent extraction are considered to be useful only for concentrated solutions[9]. Adsorption is most useful method which could be useful for Pb(II) ions removal from waste water due to its high efficiency, low maintenance costs and ease of operation[10]. Main uniqueness of adsorption behavior are evaluated by means of equilibrium isotherms and adsorption kinetics. These are very significant to understand the adsorption method for theoretical evaluation[11]. For removal of pollutants that are present in wastewater, activated carbon is most commonly used but its use has been restricted due to its high cost[12,13].

Polyaniline (PANI) is the most important and capable candidate of all intrinsically conducting polymers (ICPs), due to its high electrical conductivity, low cost, ease of synthesis, potential practical applications and good environment stability[14,15]. Polyaniline can be easily synthesized either electrochemically or chemically from acidic aqueous solutions. It can be present in different oxidation states characterized by ratio of amino nitrogen to imine[16]. A composite material is formed when two or more materials with different properties are combined together[17].

The objective of present work was to synthesize, characterize and evaluate the potential of polyaniline composites for adsorption of lead(II) from water. Plant leaves of *Madhuca longifolia* (mahwa), *Eugenia jambolana* (jamun) were selected for this study. Their polyaniline composites (PANI/ML, PANI/JL) were synthesized,characterized and used for adsorption of Pb(II).

EXPERIMENTAL

Instruments used here are: Digital balance, Chiller apparatus Caoran CAN-7000-B, FT-IR Spectrophotometer, Atomic absorption spectrophotometer (Perkin Elmer Aanalyst 100).

Chemicals used here are: aniline monomer, hydrated ferric chloride, HCl (AnalaR), DMF (PRS Panreac), acetone (BDH). Aniline was purified by distillation process before to use. The middle fraction of distillate was collected, kept under nitrogen atmosphere and stored in refrigerator.

Polymerization of aniline: It was carried out in similar way as reported earlier[16].

Product was ground well for characterization studies.

Synthesis of polyaniline composites with Mahwa and Jamun leaves (PANI/ML, PANI/JL): 10 g of pure aniline was taken in three neck flask. 75 g of ferric chloride and 375 mL of deionized was added in it. Solution temperature was settled at 0 °C. After sometime, 2 g of Jamun leaf powder was added in the reaction mixture to prepare 20 % PANI/JL composites. It was magnetically stirred for 24 h with continuous flush of nitrogen. The solution turned dark green after completion of reaction. These precipitates were filtered and washed with HCl, deionized water and finally with methanol and acetone to remove oxidants decompose product and oligomers[16,18]. These precipitates were dried in oven for 24 h. Finally this product was grinded well and stored for further experiments. Similarly PANI/ML composite was prepared using mahwa leaves powder.

Preparation of stock solution and standards: Stock solution of lead(II) was prepared by dissolving 1.59 g of lead nitrate/L of double distilled water. Further standards and working solutions of lead(II) were prepared by its dilution.

Adsorption studies: The adsorption studies of Pb(II) was carried out at 25 ± 1 °C using PANI/JL and PANI/ML composites in batch mode separately as explained earlier[18-20]. The percentage removal of metal ions in terms of adsorption was determined by eqn. 1:

$$\text{Percentage adsorption} = [(C_o - C_e)/C_o] \times 100 \qquad (1)$$

where C_o is the concentration of Pb(II) before adsorption process and C_e is concentration after adsorption process respectively[20].

Characterization of adsorbents surface functional groups by Boehm's titration: Functional groups on the surface of the adsorbents are subjected to a wide variety of inter and intra-molecular interactions. These interactions alter the surface characteristics sufficiently for adsorbent to not act like its parent material. The Boehm titration was done in order to measure the amount of acid/base taken by the adsorbent by performing a neutralizing titration. Boehm's titration is a process used to determine the number of different types of groups on adsorbent. The groups tested for using Boehm's titration are given in Table-1. 0.15 g of each adsorbent was placed in 20 mL of each of the following 0.1 M solutions: sodium hydoxide (NaOH), sodium carbonate ($NaCO_3$), sodium bicarbonate ($NaHCO_3$) and hydrochloric acid (HCl). The samples were sealed and kept at room temperature for 6 h. The solutions were then filtrated and taken for titration of the excess of the base or acid with 0.1M solutions of HCl or NaOH, respectively[21].

TABLE-1
BOEHM'S TITRATION RESULTS FOR PANI/ML

Neutralization reagent	Group neutralized	Group present (mmol)	
		PANI/ML	PANI/JL
NaOH	Carboxylic + Lactonic + Phenolic	Phenolic group is absent	Phenolic group = 0.004
$NaHCO_3$	Carboxylic + Lactonic	Lactonic group = 1.98	Lactonic group = 1.986
$NaCO_3$	Carboxylic	1.984	1.982
HCl	Basic groups	1.98	1.984

RESULTS AND DISCUSSION

(a) Boehm's titration: Boehm's titration was performed for two composites PANI/JL and PANI/ML which were further used for adsorption studies results are shown in Table-1. It shows that PANI/ML have 1.98 mmol lactonic group, 1.98 mmol basic groups, 1.984 mmol carboxylic group and phenolic groups are absent, whereas PANI/JL have 1.986 mmol lactonic group, 1.984 mmol basic groups, 1.982 mmol carboxylic group and 0.004 mmol phenolic groups. It indicated that PANI/JL had more lactonic and basic groups than PANI/ML, which in turns help in more adsorption of Pb(II) ions by chelating them.

(b) UV/visible Spectroscopic analysis: UV/visible spectra of pure polyaniline and its composites (PANI/ML, PANI/JL) are taken and their λ_{max} are shown in the Table-2 where $\lambda_{max\ 1}$ is caused by a π-π^* transition of aniline and anilinium radicals and $\lambda_{max\ 2}$ is because of π-π^* transition of quinine amine groups[22]. The absorption at 330 nm is attributed a π-π^* transition in the benzenoid ring, whereas absorption at 645 nm is ascribed to excitonic transition of benzenoid to quinonoid ring. Therefore the presence of two peaks in UV/visible spectra of samples indicate that two types of chemically non-equivalent rings are present in the polymer chain named as quinonoid and benzenoid.

TABLE-2
λ_{max} OF POLYANILINE AND ITS COMPOSITES

Sample	$\lambda_{max\ 1}$ (nm)	Absorbance	$\lambda_{max\ 2}$ (nm)	Absorbance
PANI	330	0.373	645	0.285
PANI/ML	330	0.327	635	0.227
PANI/JL	335	0.236	645	0.169

(c) FT-IR analysis: The polyaniline and its composites PANI/ML, PANI/JL were characterized by FT-IR spectroscopy. There FT-IR spectra were taken by mixing of sample with

KBr and using PRESTIGE 21 FT-IR spectrophotometer. The most important vibrational bands which allow the identification of polyaniline and its composites are given in Table-3[23]. Structural information is mainly driven from the presence or absence of characteristics absorption bands of various functional groups in the specific sample. When FT-IR spectra of composites of polyaniline (PANI/ML, PANI/JL) are compared with that of pure polyaniline, it was concluded that, (i) an intense bands in the range of 3423 cm^{-1} in the polyaniline spectrum is shifted to 3419 cm^{-1}, for PANI/JL and 3612 cm^{-1} in case of PANI/ML. This band belongs to the stretching frequency of amino group (N-H) in the protonated polyaniline[24]. (ii) The absorption band in range of 1625 cm^{-1} attributes to nitrogen bond of benzenoid to quinonoid rings because of transition of benzenoid to quinonoid. It shifts in composites towards 1647 cm^{-1}, 1625 cm^{-1}. (iii) The peaks at 1300-1290 belongs to C-N stretching of the secondary amine of polyaniline backbone[25]. These peaks shifts to 1205 cm^{-1} for PANI/ML and 1163 cm^{-1} for PANI/JL. (iv) Bands in the range of 1062-1047 are characteristic of conductive polyaniline. These are well thought-out to be a measure of degree of delocalization of electron. (v) Peaks in the range of 977-933 cm^{-1} belongs to an in plane bending vibrationof -C-H which is formed throughout protonation.

TABLE-3
INFRARED ABSORPTION BANDS OF POLYANILINE AND ITS COMPOSITES (PANI/ML, PANI/JL)

Vibrational assignment	Reference absorption bands (cm^{-1})	PANI (cm^{-1})	PANI/ML (cm^{-1})	PANI/JL (cm^{-1})
N-H stretching	3426	3423	3612	3419
N=Q=N	1577	1625	1647	1625
N=B=N	1489	1483	1510	1440
C= N stretching	1295	1292	1205	1163
Aromatic C-N-C	1121	1047	1047	1037
-C-H in plane	1030	977	972	989
-C-H out of plane	830	895	898	894

Batch adsorption experiments

(i) Effect of contact time: The phenomenon of adsorption is a time dependent process. Effect of various time intervals (10-100 min) with variation of 10 min on the percentage removal of Pb(II) using PANI/ML and PANI/JL were studied. The results are presented in Fig. 1. For both composites PANI/ML and PANI/JL maximum adsorption was observed at 90 min with PANI/ML with 95.884 % removal and in case of PANI/JL with 96.586 % removal of Pb(II). Graph indicated that after maximum removal of metal ion (Pb(II)) adsorption decreases, because all available binding sites are already occupied[22].

(ii) Effect of pH: The percentage removal of Pb(II) was studied as a function of pH in range of 1-7. Alkaline pH was avoided because it results in the precipitation of $Pb(OH)_2$. The results are shown in Fig. 2. The maximum adsorption was observed at pH 7 with PANI/ML with 97.492 % removal and at pH 2 with PANI/JL with 97.681 % removal. Below these pH values, there was decrease in adsorption because in severely acidic conditions adsorbent sites become protonated which repels the metal ions, but in basic to neutral conditions, better adsorption takes place[23].

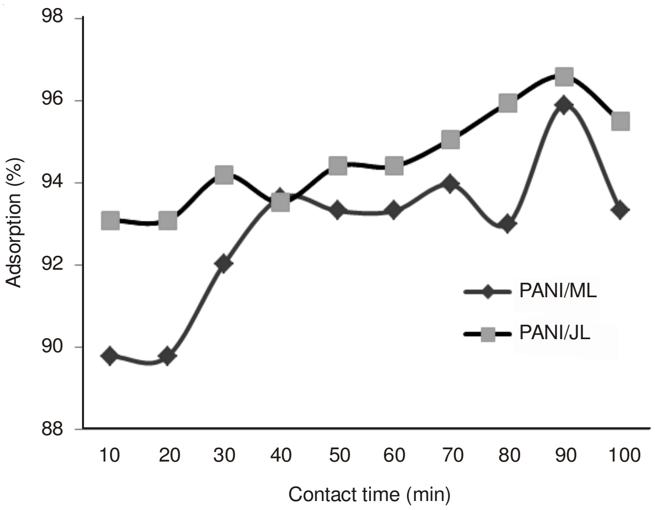

Fig. 1. Comparative graph showing effect of contact time on percentage adsorption of Pb(II)

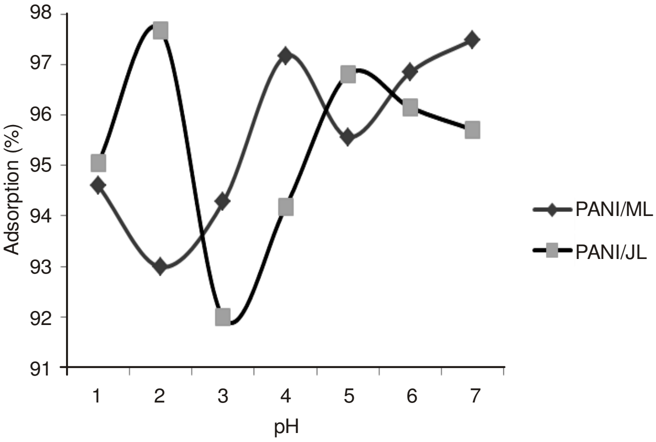

Fig. 2. Comparative graph showing effect of pH on percentage adsorption of Pb(II)

(iii) Effect of adsorbent dose: Effect of variation in adsorbent dose (0.1-1 g) on the percentage removal of Pb(II) was studied using two adsorbents PANI/ML and PANI/JL. The results are presented in Fig. 3. It was concluded that percentage removal of Pb(II) greater than before with increasing adsorbent dose of both composites. With PANI/ML composite maximum removal was at 0.8 g with 88.546 % removal of Pb(II), in case of PANI/JL it was at 0.9 g with 95.047 % removal. After maximum adsorption of metal ion percentage adsorption decreases due to coagulation of adsorbent particles, which make adsorption sites less available for binding sites[24].

(iv) Effect of temperature: The adsorption of Pb(II) on PANI/ML nad PANI/JL were observed at different temperatures ranging 20-70 °C. The results are given in Fig. 4. The maximum adsorption of Pb(II) was observed at 30 °C with PANI/ML with 92.640 %, in case of PANI/JL was at 50 °C with 96.301 % removal. Decrease in adsorption at higher temperature is due to the fact that at higher temperature molecules have less time of interaction for adsorbate with adsorbent active sites and move with greater speed[25].

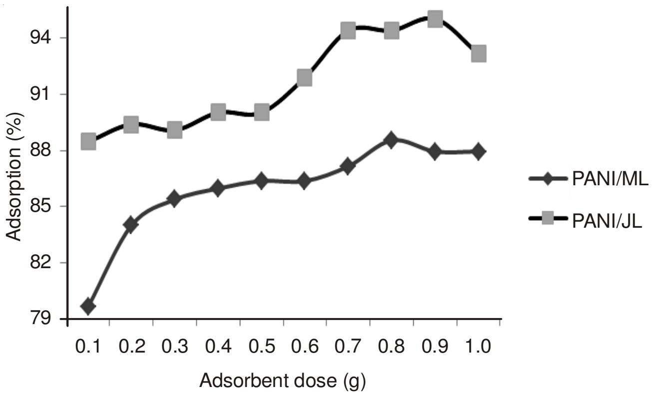

Fig. 3. Comparative graph showing effect of adsorbent dose on percentage adsorption of Pb(II)

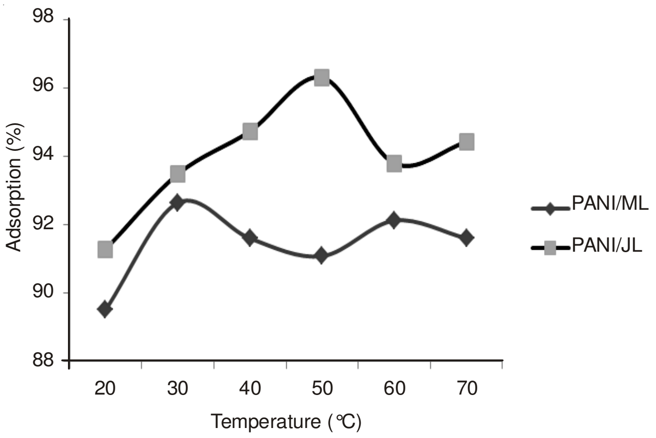

Fig. 4. Comparative graph showing effect of temperature on percentage adsorption of Pb(II)

(v) Adsorption isotherms: The optimized conditions of all factors like adsorbent dosage, contact time, pH, temperature were employed for studying the adsorption isotherms. The Langmuir isotherm is represented by the following eqn.:

$$\frac{1}{q_e} = \frac{1}{q_m \cdot bC_e} + \frac{1}{q_m} \qquad (2)$$

In Langmuir isotherm theory it is assumed that the adsorbed layer in one molecule in thickness (monolayer adsorption). The values of Langmuir constants are related to the physical properties of the system.

The value of q is calculated by using the following formula;

$$q = (C_o\text{-}C_e)V/m \qquad (3)$$

Thermodynamic parameter '$\Delta G°$' was calculated from eqn. 3:

$$\Delta G° = -RT \ln K \qquad (4)$$

where, q_m = monolayer (maximum) capacity of adsorption in mg/g b = Langmuir constant is linked to the apparent adsorption energy in L/g and $\Delta G°$ is in KJ mol^{-1}. Negative $\Delta G°$ values confirmed the spontaneous nature of adsorption. For adsorption of lead ions, the Langmuir isotherms parameters using PANI/ML and PANI/JL are given in Table-4.

For PANI/ML the value of 'q_m' was 3.891 mg g^{-1} and it was 5.917 mg g^{-1} in case of PANI/JL. For Pb(II) ions the value of 'b' was 0.268 L g^{-1} and 0.086 L g^{-1} for PANI/ML and PANI/JL, respectively. Separation factor R_L value is between 0 to 1, indicating the favorability of this process[26-28].

TABLE-4
LANGMUIR ISOTHERMAL PARAMETERS

Sample	Slope	Intercept	R^2	q_m (mg/g)	b	$\Delta G°$	R_L
PANI/ML	0.947	0.257	0.647	3.891	0.268	-3.295	0.1
PANI/JL	1.987	0.169	0.982	5.917	0.085	-6.107	0.2

The Freundlich isotherm constants studied using both adsorbents and correlation coefficients (R^2) are given in Table-5.

$$\log q_e = \log K_F + 1/n \log C_e \qquad (4)$$

whereas 'n' and 'K_F' are Freundlich isotherm constants. 'K_F' value was 0.857 and 0.500 for PANI/ML and PANIJL, respectively. For Pb(II) ions the value of 'n' was 1.524 using PANI/ML and 1.27 for PANI/JL. The higher the value of 'n' (factor related to adsorption intensity and varies with heterogeneity of the material), higher will be the affinity and heterogeneity of adsorbent sites. The correlation coefficient (R^2) is for Langmuir isotherm is greater in case of PANI/JL, which suggests this isotherm holds good in this case. It means more monolayer chemisorption occurred as compared to multilayer physiosorption. *Vice versa* is true using PANI/ML composites.

TABLE-5
FREUNDLICH ISOTHERMAL PARAMETERS

Sample	Slope	Intercept	R^2	K_F	n
PANI/ML	0.656	-0.067	0.812	0.857	1.524
PANI/JL	0.786	-0.301	0.974	0.500	1.27

Conclusion

The result of characterization and adsorption showed that PANI/JL is better adsorbent for removal of Pb(II) ions from water as compared to the PANI/ML. Negative value of $\Delta G°$ shows that adsorption process was spontaneous. Using optimized conditions, maximum removal capacity of Pb(II) from water is 3.891 mg g^{-1} for PANI/ML and 5.917 mg g^{-1} for PANI/JL.

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