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Adsorptive Eradication of Cadmium(II) from Water Using Biocomposites of Polyaniline with *Madhuca longifolia* and *Eugenia jambolana* Leaves Powder

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Adsorptive eradication of cadmium(II) from water was studied in batch mode using novel synthesized polyaniline/*Madhuca longifolia* and polyaniline/*Eugenia jambolana* composites. The optimum conditions of sorption of cadmium(II) solution with polyaniline/*Madhuca longifolia* composite were: 0.6 g/50 mL adsorbent dose, 40 min contact time, 5 pH and 50 °C temperature. Whereas for polyaniline/*Eugenia jambolana* composites, these conditions were:adsorbent dose 0.6 g/50 mL, 80 min contact time, 6 pH and 30 °C temperature. Langmuir isotherm model was applicable in both cases, indicating that monolayer chemisorptive removal of metal ions occurred more on homogeneously distributed binding sites of composites as compared to physiosorption on multilayers binding sites. The maximum adsorption capacity of polyaniline/*Madhuca longifolia* composite was found to be 0.498 mg/g, while in case of polyaniline/*Eugenia jambolana* was 0.444 mg/g. The feasibility and spontaneity of this process was shown by negative value of ΔG^o. Freundlich constant K_F values were: 8.89×10^{-5} and 4.47×10^{-5} $mgL^{-1/n}$ $L^{1/n}$ g^{-1} for polyaniline/*Madhuca longifolia* and polyaniline/*Eugenia jambolana* respectively. Results show that polyaniline/*Madhuca longifolia* is better adsorbent for cadmium(II) removal and shows more adsorption than polyaniline/*Eugenia jambolana*. Polyaniline/*Madhuca longifolia* and polyaniline/*Eugenia jambolana* were characterized by UV/visible spectroscopy, FT-IR spectroscopy and Boehm's titration.

Keywords: Polyaniline, *Madhuca longifolia*, *Eugenia jambolana*, Composites, Cadmium(II), Adsorption.

INTRODUCTION

The removal of toxic metals from water by adsorption is a hot topic in these days. In this study, cadmium(II) is focused. It is found in ores together with zinc, copper and lead. Volcanic activity is one of the natural reasons for its temporary increase in environmental[1]. It is toxic for plant growth and induces lethal effects on plants including leaf chlorosis, change in enzymes activity, inhibits roots and shoots growth, affects nutrient uptake and homeostasis[2-4]. Its salts impurities in water usually comes from electroplating, stabilizing plastics, batteries, alloy manufacturing, mining and metallurgical processes, pigment and high-phosphate fertilizers[5-10].

Chemical precipitation, ion exchange, membrane systems, desalination, phytoremediation and adsorption are different heavy metal treatment methods[11,12]. The last one offers to the treatment of waste-waters containing moderate and low concentrations of metal ions. In this process, activated carbon is the standard adsorbent and due to its high-cost, production of its low cost alternatives has been focused by researcher in recent years. Various industrial and metallurgical wastes and by-products, biological wastes, natural substances and minerals have been considered as adsorbents for the wastewater treatment[13].

In this research work, polyaniline/*Madhuca longifolia* leaves (PANI/ML) and polyaniline/*Eugenia jambolana* leaves (PANI/JL) were synthesized, characterized and employed for the adsorptive eradication of cadmium(II) from water in batch mode. Polyaniline (PANI) was initially discovered in 1834 by Runge and it was referred to aniline black (Fig. 1). There are different methods that can be in employment to synthesize conducting polymers such as: electrochemical oxidation of monomers and chemical synthesis[14]. Amongst conducting polymers, polyaniline is used more in LEDs, transparent electrodes, EMR shielding, corrosion protection of metals, battery gas and humidity sensing purposes. It reports as high biocompatible because of its accommodating surface behaviour[15-18].

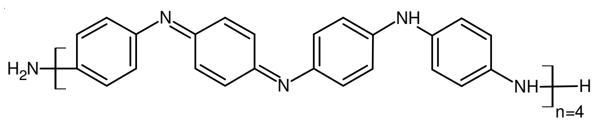

Fig. 1. General molecular structure of polyaniline

EXPERIMENTAL

Aniline monomer, hydrated ferric chloride, nitrogen gas, HCl, distilled water, methanol and acetone were used. Aniline was purified by distillation process before to use and stored in refrigerator. *Madhuca longifolia* commonly known as Mahwa and *Eugenia jambolana* (*Syzygiumcumini*, or Jamun) plant leaves were collected from home institute and dried in sunlight after washing. Dried leaves were grinded to make fine powder of 60 mesh size, which was further used for synthesizing polyaniline composites.

Synthesis of adsorbents (polyaniline and its composites polyaniline/*Madhuca longifolia* and polyaniline/*Eugenia jambolana*): It was carried out in similar fashion as reported earlier by our research group using leaf powder instead of bran or husk material[19-21]. General scheme is shown in Fig. 2.

Stock and standard solution of cadmium: 0.21 g of cadmium nitrate was dissolved in some quantity of double distilled water and the diluting up to 1000 mL for making 100 ppm stock solution of cadmium(II). Further standards and working solutions were prepared by its required calculated dilution.

Adsorption studies: The adsorption studies of cadmium(II) was carried out at 25 ± 1 °C using polyaniline/*Eugenia jambolana* and polyaniline/*Madhuca longifolia* composites in batch mode separately in similar fashion as described earlier[19-21]. The %age removal of metal ions is determined by eqn. 1:

$$\%\text{age adsorption} = [(C_o-C_e)/C_o] \times 100 \quad (1)$$

All the experiments were performed in triplicates andaverage values were taken with the experimental error in the range of 0.5-2.5 %.

Boehm's titration for determination of oxygen containing functional groups: Functional groups on the surface of the adsorbents are subjected to a wide variety of inter- and intra-molecular interactions. These interactions modify the surface characteristics of adsorbent in such a way that they do not act like its parent material. The boehm titration was done in order to measure the amount of acid/base taken by the adsorbent for neutralization by performing a neutralizing titration. It is a process used to determine the number of different types of groups on adsorbent. For this purpose, 0.15 g of each adsorbent was placed in 20 mL of each of the following 0.1 M solutions *i.e.*, NaOH, Na_2CO_3, $NaHCO_3$ and HCl. The samples were sealed and kept at room temperature for 8 h. The solutions were then filtrated and taken for titration of the excess of the base or acid with 0.1 M solutions of HCl or NaOH, respectively. The neutralization of sample with NaOH, Na_2CO_3, $NaHCO_3$ and HCl was used to determine the number of phenolic, lactonic, carboxylic and basic groups, respectively. The results are presented in Table-1[16].

RESULTS AND DISCUSSION

Characterization of adsorbents

Boehm's titration: Boehm's titration was performed for two composites polyaniline/*Eugenia jambolana* and polyaniline/*Madhuca longifolia* which were further used for adsorption studies results are shown in Tables 1 and 2. Table-1 shows that polyaniline/*Madhuca longifolia* contain 1.98 mmol lactonic group, 1.98 mmol basic groups, 1.984 mmol carboxylic group and phenolic groups are absent. Table-1 shows that polyaniline/*Eugenia jambolana* contains 1.986 mmol lactonic group, 1.984 mmol basic groups, 1.982 mmol carboxylic group and 0.004 mmol phenolic groups.

UV/visible spectroscopy: UV-visible spectra of pure polyaniline and its composites (polyaniline/*Madhuca longifolia*, polyaniline/*Eugenia jambolana*) were taken and presented in Fig. 3. The λ_{max} are shown in the Table-2. Here λ_{max1} is caused by n-π* transition of aniline and anilinium radicals and λ_{max2} is because of n-π* transition of quinine-imine groups[20-22]. The absorption at 330 nm is attributed to n-π* transitionin the benzenoid ring, whereas absorption at 645 nm is ascribed to excitonic transition of benzenoid to quinoid ring. Thus the presence of two peaks in UV/visible spectra of samples indicated the presence of two types of chemically non-equivalent rings in the polymer chain named as benzenoid and quinoid. They were further confirmed by recording FT-IR spectra of samples.

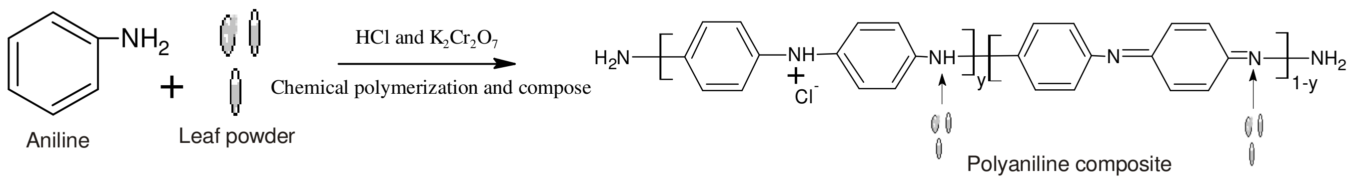

Fig. 2. Schematic synthesis of polyaniline composites

TABLE-1
BOEHM'S TITRATION RESULTS FOR POLYANILINE/*Madhuca longifolia* (PANI/ML) AND POLYANILINE/*Eugenia jambolana* (PANI/JL)

Neutralizing reagent	Group neutralized	Group present in PANI/ML (mmol)	Group present inPANI/JL (mmol)
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	1.980	1.984

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

Sample	λ_{max1} (nm)	Absorbance	λ_{max2} (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

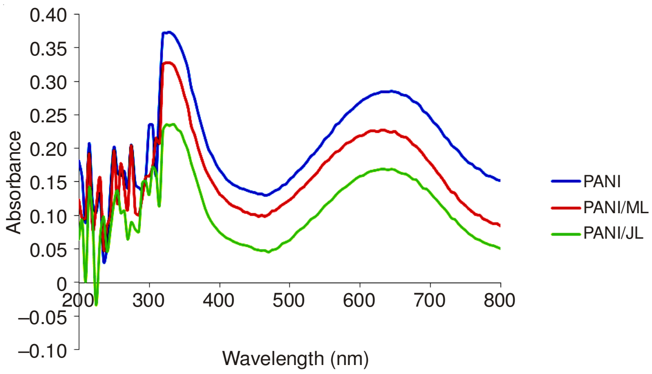

Fig. 3. Comparative graph of UV-visible analysis for polyaniline (PANI) and its composites

FT-IR characterization: The polyaniline and its composites polyaniline/*Madhuca longifolia* and polyaniline/*Eugenia jambolana* were characterized by FT-IR spectroscopyby mixing samples with KBr and using PRESTIGE 21 FT-IR spectrophotometer. The most important vibrational bands which allow the identification of polyaniline and its composites are mentioned in Table-3.[20-22]. 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 were compared with that of pure polyaniline, it was concluded that,

- Intense bands in the range of 3423 cm^{-1} in the polyaniline spectrumis shifted to 3419 cm^{-1} for polyaniline/*Eugenia jambolana* and 3612 cm^{-1} in case of polyaniline/*Madhuca longifolia*. This band belongs to the stretching frequency of amino group (N-H) in the protonated polyaniline.
- The absorption band in range of 1625 cm^{-1} attributes to nitrogen bond of benzenoid to quinoid rings because of transition of benzenoid to quinoid. It shifts in composites towards 1647 and 1625 cm^{-1}.
- The peaks at 1300-1290 are assigned to C-N stretching of the secondary amine of polyaniline backbone[25]. These peaks shift to 1205 cm^{-1} for polyaniline/*Madhuca longifolia* and 1163 cm^{-1} for polyaniline/*Eugenia jambolana*.
- Bands in the range of 1047-1062 are characteristic of conductive polyaniline. These are considered to be a measure of degree of delocalization of electron.
- Peaks in the range of 977-933 cm^{-1} can be assigned to an in plane bending vibration of C-H which formed during protonation[20-22].

After characterizing polyaniline composites, they were employed for adsorption studies of cadmium(II) in batch mode for optimizing operational parameters.

Batch adsorption experiments

Effect of contact time: The phenomenon of adsorption is a time dependent process. The effect of various time intervals on the %age removal of cadmium(II) using polyaniline/*Madhuca longifolia* and polyaniline/*Eugenia jambolana* were studied. The results are presented in Fig. 4. For polyaniline/*Madhuca longifolia* maximum adsorption was observed at 40 min with 18.707 % removal and in case of polyaniline/*Eugenia jambolana* it was at 80 min with 14.725 % removal of cadmium(II). Graph shows that after maximum removal of cadmium(II) ions, adsorption decreases because all available binding sites are already occupied[20-24]. For cadmium(II) removal, polyaniline/*Madhuca longifolia* shows more adsorption than polyaniline/*Eugenia jambolana*.

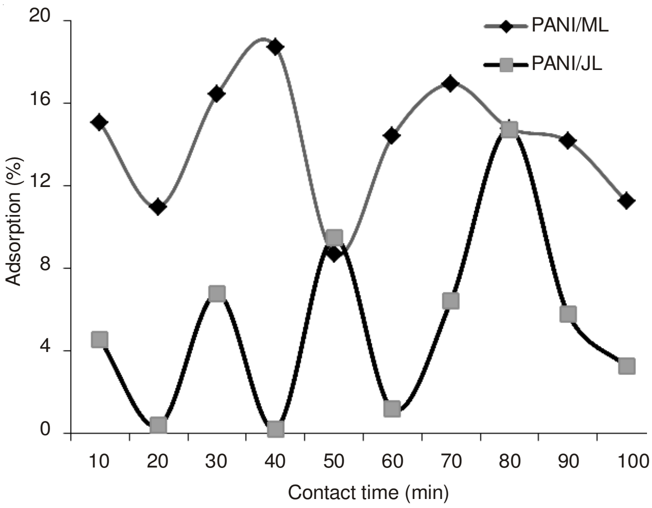

Fig. 4. Graph showing effect of contact time on %age adsorption of cadmium(II) by polyaniline/*Madhuca longifolia* (PANI/ML) and Polyaniline/*Eugenia jambolana* (PANI/JL)

Effect of pH: Effect of pH is an important parameter that controls the adsorption process. The %age removal of cadmium(II) was studied as a function of pH in range of 1-7. Alkaline pH was avoided because it results in the precipitation of $Cd(OH)_2$. The results are shown in Fig. 5. With polyaniline/*Madhuca longifolia*, the maximum adsorption was observed at pH 5 with 24.537 % removal and at pH 6 with polyaniline/*Eugenia jambolana* with 22.534 % 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]. For Cd(ll) removal polyaniline/*Madhuca longifolia* shows more %age adsorption as compare to polyaniline/*Eugenia jambolana*.

TABLE-3
INFRARED ABSORPTION BANDS OF POLYANILINE (PANI), POLYANILINE/*Madhuca longifolia* (PANI/ML) AND POLYANILINE/*Eugenia jambolana* (PANI/JL) [Ref. 19-21]

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≡Nstretching	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

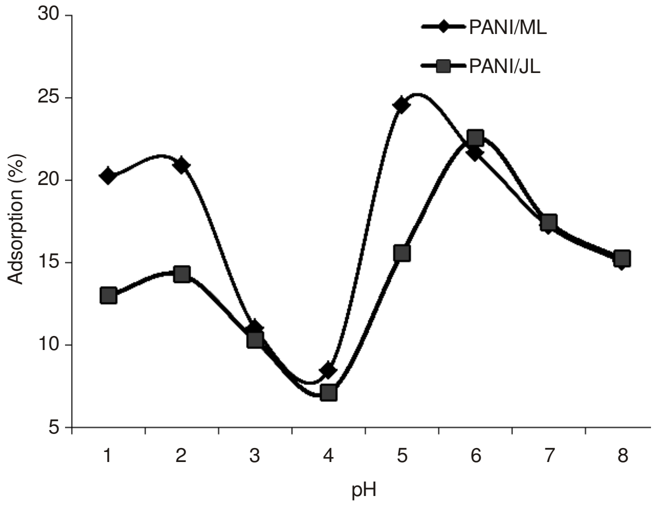

Fig. 5. Graph showing effect of pH on %age adsorption of cadmium(II) by polyaniline/*Madhuca longifolia* (PANI/ML) and polyaniline/*Eugenia jambolana* (PANI/JL)

Effect of adsorbent dose: The effect of variation in adsorbent dose on the percentage removal of Cd(ll) was studied using two adsorbents polyaniline/*Madhuca longifolia* and polyaniline/*Eugenia jambolana*. The results are presented in Fig. 6. It was observed that %age removal of cadmium(II) increased with increasing adsorbent dose of both composites. With polyaniline/*Madhuca longifolia* composite maximum removal was at 0.6 g with 35.546 % removal of cadmium(II), in case of polyaniline/*Eugenia jambolana* it was at 0.6 g with 29.865 % removal. After maximum adsorption of metal ion %age adsorption decreases due to coagulation of adsorbent particles, which make adsorption sites less available for binding sites[24]. Polyaniline/*Madhuca longifolia* shows more %age adsorption for cadmium(II) as compared to polyaniline/*Eugenia jambolana*.

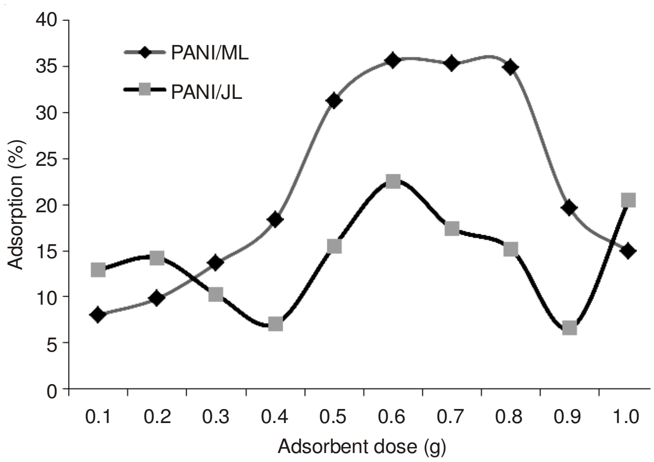

Fig. 6. Graph showing effect of adsorbent dose on %age adsorption of cadmium(II) by polyaniline/*Madhuca longifolia* (PANI/ML) and polyaniline/*Eugenia jambolana* (PANI/JL)

Effect of temperature: The adsorption of cadmium(II) on polyaniline/*Madhuca longifolia* and poly-aniline/*Eugenia jambolana* were observed at different temperatures ranging 20-70 °C. The results are given in Fig. 7. The maximum adsorption of cadmium(II) was observed at 50 °C with polyaniline/*Madhuca longifolia* with 11.736 %, in case of polyaniline/*Eugenia jambolana* was at 30 °C with 10.104 % removal. Decrease in adsorption at elevated temperature is due to the fact that molecules move with greater speed and less time of interaction was available for adsorbate with adsorbent active sites. For cadmium(II), polyaniline/*Madhuca longifolia* shows more %age removal as compared to polyaniline/*Eugenia jambolana*.

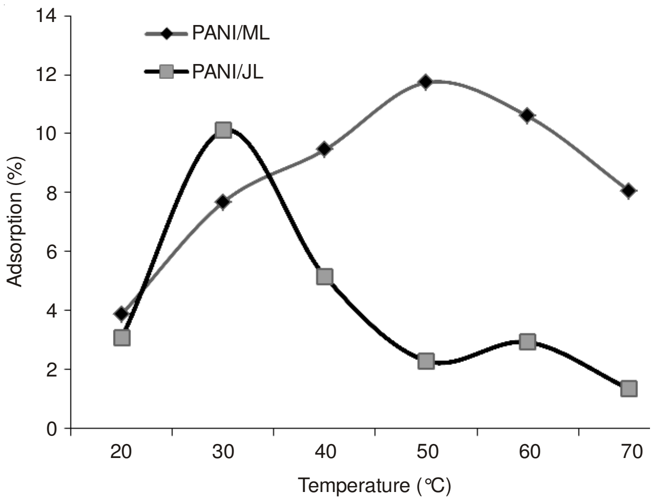

Fig. 7. Graph showing effect of temperature on %age adsorption of cadmium(II) by polyaniline/*Madhuca longifolia* (PANI/ML) and polyaniline/*Eugenia jambolana* (PANI/JL)

Adsorption isotherms: Optimized conditions for removal of cadmium(II) by polyaniline/*Madhuca longifolia* and polyaniline/*Eugenia jambolana* were applied simultaneously to 30-70 ppm metal ion concentration for studying adsorption isotherms.

Langmuir model: In Langmuir isotherm theory it is assumed that monolayer adsorption occurred at homogenously distributed active sites. The values of Langmuir constants are related to the physical properties of the system. It can be represented by the following equation;

$$\frac{1}{q} = \frac{1}{q_m\, bC_e} + \frac{1}{q_m} \quad (2)$$

The value of q is calculated using the following formula;

$$q = \frac{(C_o - C_e)V}{m} \quad (3)$$

where, q_m = monolayer (maximum) capacity of adsorption in mg g^{-1}, b = Langmuir constant related to the apparent adsorption energy in L g^{-1} and ΔG^o is in KJ mol^{-1}. They are shown in Table-4. For polyaniline/*Madhuca longifolia* the value of 'q_m' was 0.498 mg g^{-1} and it was 0.444 mg g^{-1} in case of polyaniline/*Eugenia jambolana*. Table-5 is showing the comparison of these novel composites of polyaniline for removing cadmium(II) with previously reported adsorbents[19,25-27]. It clearly reflects the more capacity of these composites for using them as adsorbents. The correlation coefficient (R^2) is near to one, which suggests the Langmuir isotherm is applicable. The Langmuir isotherm parameter 'q_m' was used to determine the specific surface area (S_L, m^2/g) of the adsorbent available for adsorption by using the following eqn. 4[19]:

TABLE-4
LANGMUIR ISOTHERMAL PARAMETERS FOR ADSORPTION OF CADMIUM(II) USING POLYANILINE/*Madhuca longifolia* (PANI/ML) AND POLYANILINE/*Eugenia jambolana* (PANI/JL)

Sample	Slope	Intercept	R^2	q_m(mg/g)	b	ΔG°	R_L
PANI/ML	68.44	-2.009	0.983	0.498	0.0293	-8.746	0.406
PANI/JL	81.33	-2.254	0.997	0.444	0.0276	-8.894	0.420

TABLE-5
COMPARISON OF MAXIMUM ADSORPTION CAPACITY WITH REPORTED ADSORBENTS FOR REMOVAL OF CADMIUM(II)

Adsorbent	Maximum Adsorption capacity (q_m) mg g^{-1}	Reference
Polyaniline	0.1650	19
Polyaniline/saw dust composite	4.7390	19
Polyaniline/rice husk composite	5.1280	19
Sodium bicarbonate treated old newspaper	1.4405	25
Pine bark char	0.3400	26
Bagasse fly ash	2.0000	27
Polyaniline/*Madhuca longifolia* leaves composite	0.4980	(Present study)
Polyaniline/*Eugenia jambolana* leaves composite	0.4440	(Present study)

$$S_L = \frac{N_A A q_m}{M} \quad (4)$$

The molecular mass of cadmium is 112 and the cross sectional area is 3.73 Å^2 (the radius of cadmium(II) ions for close packed monolayer is 1.09 Å. The specific surface areas of (polyaniline/*Madhuca longifolia*) and (polyaniline/*Eugenia jambolana* composites were calculated to be 9.98 and 8.90 m^2/g, respectively. These results clearly indicate that polyaniline composites have larger surface area for adsorption.

Thermodynamic parameter 'ΔG°' was calculated from eqn. 4 using inverse of Langmuir parameter '*b*' as K:

$$\Delta G^o = -RT \ln K \quad (5)$$

Negative values of Gibb's free energy are indicating the feasibility of this process and exothermic nature of adsorption. Langmuir parameter '*b*' is used for determining a dimensionless separation factor constant 'R_L' by using eqn. 6[28].:

$$R_L = \frac{1}{(1+bC_o)} \quad (6)$$

R_L < 1 represents favorable process. Adsorption of cadmium(II) ions is more favorable with polyaniline/*Madhuca longifolia* as compared to polyaniline/*Eugenia jambolana* composites because its R_L value is less.

Freundlich model: In Freundlich isotherm theory, it is assumed that multilayer physiosorption occurred on heterogeneously distributed active sites. It was plotted using following standard straight-line eqn. 7:

$$\log q = \log K + \frac{1}{n} \log C_e \quad (7)$$

The isotherm constants studied using both composites and correlation coefficients (R^2) are shown in Table-6. The correlation coefficient (R^2) is near to one, which suggests that this model is applicable.

Mechanism of cadmium(II) adsorption: The possible mechanism of cadmium(II) adsorption on polyaniline composites is shown in Fig. 8[19]. It is a generalized fact that nitrogen containing functional groups can act as adsorption sites for metal ions. It is indicated that A^- is anion doped in polyaniline/*Madhuca longifolia* and polyaniline/*Eugenia jambolana* during the synthesis by chemical oxidation process of aniline. The applicability of Langmuir isotherm on equilibrium data confirmed that the removal of cadmium(II) occurred more by chemisorption in monolayer fashion on the surfaces of polyaniline/*Madhuca longifolia* and polyaniline/*Eugenia jambolana* composites.

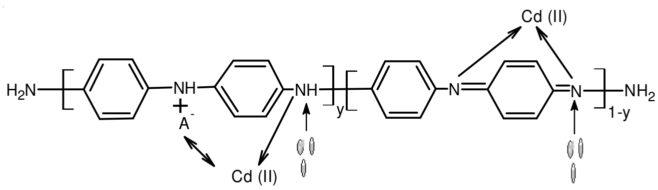

Fig. 8. Mechanism for Cd(II) removal by polyaniline/*Madhuca longifolia* (PANI/ML) and polyaniline/*Eugenia jambolana* (PANI/JL) composites

Conclusion

It was observed that Polyaniline bio-composites can be effectively employed for heavy metal ions adsorption. The trend of adsorption of cadmium(II) ions with these adsorbents was decreased in the following order:

Polyaniline/*Madhuca longifolia* >
Polyaniline/*Eugenia jambolana*

The maximum adsorption capacities of polyaniline/*Madhuca longifolia* composites is 0.498 mg/g, while in case of polyaniline/*Eugenia jambolana* it was 0.444 mg/g in optimized conditions. Langmuir and Freundlich models applicability indicated that both physiosorption and chemisorption

TABLE-6
FREUNDLICH ISOTHERMAL PARAMETERS FOR ADSORPTION OF CADMIUM(II) USING POLYANILINE/*Madhuca longifolia* (PANI/ML) AND POLYANILINE/*Eugenia jambolana* (PANI/JL)

Sample	Intercept	R^2	K_F ($mg^{1-1/n} L^{1/n} g^{-1}$)	n
PANI/ML	-4.051	0.928	8.89×10^{-5}	0.33
PANI/JL	-4.323	0.976	4.47×10^{-5}	0.32

mode of removal of cadmium(II) ions by composites increased as compared to simple polyaniline (0.165 mg g^{-1}, as investigated earlier[19]). So these composites are useful for adsorptive removals of cadmium(II) ions.

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