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# Isothermal Investigation of Copper(II) and Nickel(II) Adsorption from Water by Novel Synthesized Polyaniline Composites with *Polyalthia longifolia* and *Alastonia scholaris* Dried Leaves

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The preparation of polyaniline composites with *Polyalthia longifolia* and *Alastonia scholaris* was done in this research work. These composites were characterized by UV/visible and FT-IR spectroscopy and after that they were employed for adsorptive removal of Cu(II) and Ni(II) from aqueous medium on batch scale. The suitability of the data was tested with Langmuir and Freundlich models of isotherm. Maximum sorption capacities of polyaniline/*Alastonia scholaris* composites for removing Ni(II) and Cu(II) are: 16.17 and 31.25 mg/g respectively, while in case of polyaniline/*Polyalthia longifolia* composites for removing Ni(II) and Cu(II) are: 11.64 and 28.21 mg/g respectively. Thermodynamic studies showed that sorptive removal of Cu(II) and Ni(II) by these composites occur spontaneously because *Polyalthia longifolia* and *Alastonia scholaris* modified the morphology of polyaniline by preventing its aggregation and improving its adsorption capacity.

**Key Words: Adsorption, Polyaniline, Composites, Cu(II), Ni(II), Isotherms.**

## INTRODUCTION

In this research work, copper(II) and nickel(II) were removed from aqueous medium by novel synthesized composites of polyaniline with dried leaf mulch of *Polyalthia longifolia* and *Alastonia scholaris*. Adsorption process is an effective and economical alternative of customarily used contaminated water treatment methodologies like coagulation, electro-dialysis, ion exchange. Researchers are trying to prepare adsorbents using agro-waste materials from their indigenous resources, so that import cost can be decreased and shelf life can be increased. Polyaniline composites have these advantages along with ease of desorption for regeneration and reuse of material[1-5].

Polyaniline is a well-known conducting polymer due to its low cost, environmental stability, high conductivity, specific doping/de-doping mechanism and additional exceptional integrative properties[6,7]. Its general structure is given in Fig. 1. It is synthesized from aniline by polymerization in acidic media in the presence of oxidizing agent. Highly conducting doped forms can be obtained by protonic acid or oxidative doping. It shows electro-chromic behaviour (yellow-green-violet), dependent on its oxidation state and/or pH.[8] It exists in different forms exhibiting variation in physical and chemical properties which depend upon the degree of oxidation of nitrogen atoms, *i.e.* pernigraniline, leucoeeralidine and/oremeraldine base[9,10]. The variety in colour shades, charges and stereo-conformations of polyaniline make it suitable for production of electrically conducting yarns, electro-magnetic protective shields, antistatic coatings and bendable electrodes[11-13]. Synthesizing its composites with agro-waste materials make it a suitable adsorbent for removal of heavy metal ions from aqueous medium like Cr(VI), Pb(II), Hg(II), organic pollutants like humic acid and dyes[14-17]. The advantages of polyaniline/agro-waste material composites are their stability, more adsorption capacity and ease of desorption.

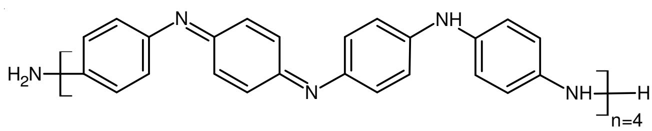


Fig. 1. General molecular structure of polyaniline

Copper(II) and nickel(II) are found as contaminants in food, like Cu(II) in shellfish, liver, mushrooms, nuts and chocolate and Ni(II) in vegetable ghee and other dyed foods. Higher concentration up to 130 mg $L^{-1}$ of Ni(II) were found in waste-water coming from mine drainage, table-ware plating and metal-finishing industries[18-27]. These metals are essential for human life but they are potentially toxic as well, especially their excessive intake in human beings cause diarrhoea, pulmonary fibrosis, severe mucosal irritation, capillary mutilation, hepatic and renal impairment and central nervous problems. Wilson's disease is caused by Cu(II) excess in body, in which it started depositing in various human tissues like: liver, pancreas and myocardium. Recommended maximum permissible limits by W.H.O. for Cu(II) and Ni(II) in drinking water are 1.5 and 0.02 mg $L^{-1}$ respectively[28-38]. So their removal from waste water is essential by adopting economical and efficient methodology like adsorption. This study is carried out for investigation the adsorption capacities of new adsorbents made from polyaniline, along with desorption study, so that adsorbents can be reused on industrial scale after regeneration.

## EXPERIMENTAL

Aniline monomer and ferric chloride were purchased from Riedel-deHaën. The middle fraction of distillate was collected, kept under nitrogen atmosphere and stored in refrigerator. Impure aniline was purified by distillation process. Distillation of aniline carried out at 180 ºC. Pure aniline was collected in a flask and stored in refrigerator at 4 ºC. To protect aniline from moisture, flask was covered with aluminium foil. Hydrochloric acid and DMF was purchased from Merck. Acetone was purchased from BDH. Flame atomic absorption spectrophotometer (Perkin Elmer AAnalyst 100) was used for quantification of metal ions and UV/visible spectrometer (Labomed, Inc. Spectro UV-visible double beam UVD = 3500) and FT-IR (Perkin Elmer Spectrum RX-I employing ATR cell) were used for structural analysis of composites.

**Preparation of adsorbents (Synthesis of polyaniline composites with *Alastonia scholaris* and *Polyalthia longifolia* leaves):** 10 g of pure distilled aniline was taken in three necked flask. 75 g of ferric chloride and 375mL of deionized water was added in it. After sometime, 2 g of *Alstonia scholaris* dried leaf powder was added in the reaction mixture for making 20 % polyaniline/*Alastonia scholaris* composites. This solution was kept at 25 ºC with gentle stirring for 24 h with a continuous flush of nitrogen. The solution turned dark green at the completion of reaction. After specified time, dark green precipitates were filtered and washed with HCl, deionized water, methanol and finally with acetone, in order to remove oxidants, decomposition product and oligomers[39,40]. These precipitates were dried in oven for 24 h. Finally this product was grinded well and subjected for FT-IR and UV/visible spectrometric analysis. Similarly polyaniline/*Polyalthia longifolia* composites were prepared using *Polyalthia longifolia* leaf powder instead of *Alstonia scholaris* leaf powder in above procedure. Polyaniline sample were prepared for comparing structural changes occurring during composite formation by similar methodology as described earlier without adding leaf powder during polymerization. The % age yield of adsorbents was calculated using following relationship[41]:

$$\text{Yield (\%)} = \frac{\text{Amount of PANI (g) produced}}{\text{Amount of PANI (g) charged}} \times 100 \quad (1)$$

and results are given in Table-1. The generalized chemical reaction is given in Fig. 2.

**Adsorption Studies:** The adsorption studies of Cu(II) and Ni(II) were done at 25 ± 1 ºC using polyaniline/*Polyalthia longifolia* and polyaniline/*Alastonia scholaris* composites in batch mode separately.10 mmol HCl/NaOH were used for pH adjustment. The effect of various conditions on the rate of adsorption process was explored by varying contact time (5-60 min), adsorbent amount (0.1- 1.5 g), initial pH of the solution (1-7) and temperature (20-70 ºC) using 50 mL of 50 ppm ($C_o$) solutions. After attaining the adsorption equilibrium, all these mixtures were filtered and remaining solutions were analyzed with AAS for residual metal ion concentration ($C_e$) at resonance wavelengths 324.8 nm and 232 nm for Cu(II) and Ni(II) correspondingly. The % age removal of metal ions in terms of adsorption was calculated from eqn. 2:[40-43].

$$\text{Adsorption (\%)} = [(C_o - C_e)/C_o] \times 100 \quad (2)$$

**Desorption studies:** For regeneration of used polyaniline/*Polyalthia longifolia* and polyaniline/*Alastonia scholaris* composites, desorption of Cu(II) and Ni(II) was carried out in batch mode using 10 mM solution of HCl, $HNO_3$ and $H_2SO_4$. By comparing metal ions desorbed ($q_{des}$) to the metal ions adsorbed (q), % age desorption was determined by eqn. 3:[43].

$$\text{Desorption} = q_{des}/q \times 100 \quad (3)$$

TABLE-1
PERCENTAGE YIELD OF PRODUCT OBTAINED

| Compound | Yield (%) |
|---|---|
| Polyaniline | 68 |
| Polyaniline/*Alastonia scholaris* | 78 |
| Polyaniline/*Polyalthia longifolia* | 83 |

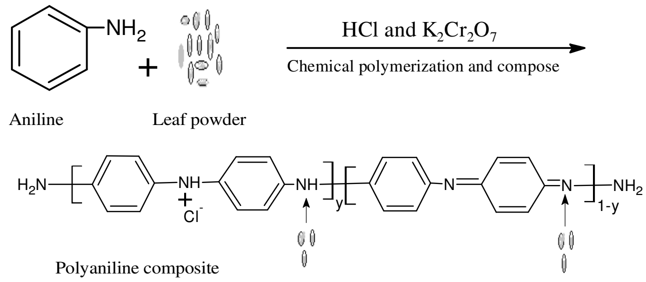


Fig. 2. Schematic synthesis of polyaniline composites

## RESULTS AND DISCUSSION

Polyaniline/*Alastonia scholaris* and polyaniline/*Polyalthia longifolia* composites of different compositions were prepared and characterized by recording their UV/visible and FT-IR spectra. Then adsorption studies were carried out with synthesized waste water containing Cu (II) and Ni(II) separately.

**UV/visible spectroscopic analysis:** UV/visible spectra of polyaniline and its composites, *i.e.* polyaniline/*Alastonia scholaris* and polyaniline/*Polyalthia longifolia* were recorded and their $\lambda_{max}$ are shown in Table-2 where $\lambda_{max1}$ is caused by $\pi$-$\pi^*$ transition of aniline and anilinium radicals and $\lambda_{max2}$ is because of $\pi$-$\pi^*$ transition of quinine amine groups. The absorption at 230 nm is attributed to $\pi$-$\pi^*$ transition in the benzeneoid ring, whereas the 605 nm peak is ascribed to excitonic transition of benzenoid to quinoid ring. Thus the presence of two peaks in UV/visible spectra of samples indicates the occurrence of two types of chemically non- equivalent rings in polymer chain termed as benzoined and quinoid[39].

**FT-IR spectroscopic analysis:** The infrared spectra of all adsorbents were recorded and given in Figs. 3-5. Charac-

TABLE-2
$\lambda_{max}$ OF POLYANILINE (PANI) AND ITS COMPOSITES WITH *Alastonia scholaris* (PANI/A.S) AND *Polyalthia longifolia* (PANIA/P.L) LEAVES

| Sample code | $\lambda_{max\,1}$(nm) | $\lambda_{max\,2}$(nm) |
|---|---|---|
| PANI | 230 | 605 |
| PANI/A.S | 248 | 560 |
| PANI/P.L | 296 | 620 |

teristic vibrational frequencies of specific functional groups of polyaniline are compared in Table-3 with polyaniline composites for observing structural changes occurring during composites formation.

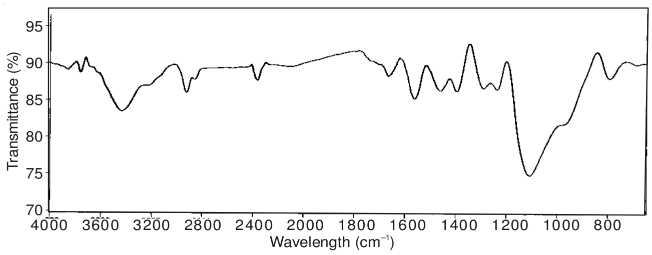


Fig. 3. FT-IR spectrum of polyaniline

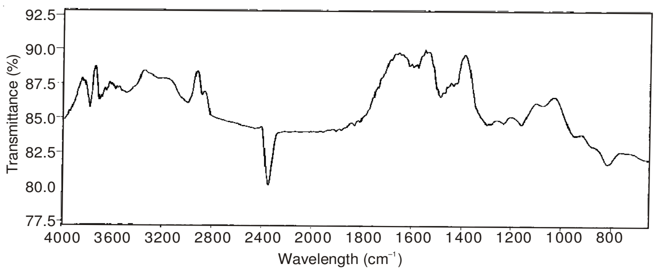


Fig. 4. FT-IR spectrum of polyaniline composites with *Alstonia scholaris* leaves

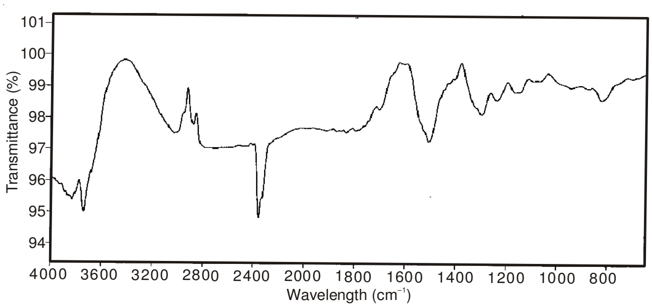


Fig. 5. FT-IR spectrum of polyaniline composites with *Polyalthia longifolia* leaves

TABLE-3
INFRARED ABSORPTION BANDS OF POLYANILINE (PANI) AND ITS COMPOSITES WITH *Alastonia scholaris* (PANI/A.S) AND *Polyalthia longifolia* (PANIA/P.L) LEAVES

| Vibrational assignments | Reference absorption bands ($cm^{-1}$) | PANI ($cm^{-1}$) | PANI/ A.S ($cm^{-1}$) | PANI/P.L ($cm^{-1}$) |
|---|---|---|---|---|
| N-H stretching | 3426 | 3431 | 3487 | 3014 |
| N=Q=N | 1577 | 1562 | 1577 | 1506 |
| N=B=N | 1489 | 1458 | 1485 | 1300 |
| -C≡N stretching | 1295 | 1290 | 1234 | 1242 |
| Aromatic C-N-C | 1121 | 1236 | 1161 | 1153 |
| C-H in plane | 1030 | 1109 | 1078 | 1072 |
| C-H out of plane | 830 | 792 | 813 | 823 |

When FT-IR spectra of composites of polyaniline/*Alastonia scholaris* and polyaniline/*Polyalthia longifolia* are compared with that of pure polyaniline, it is concluded that, the intense bands in the range of 3431 $cm^{-1}$ in polyaniline spectrum is shifted towards 3487 and 3014 $cm^{-1}$. These bands belong to the stretching frequency of amino group (N-H) in the protonated polyaniline. The absorption band in the range of 1562 $cm^{-1}$ attributes to nitrogen bond conversions occurring in benzenoid to quinoid ring transformations. It shifts in composites towards 1577and 1506 $cm^{-1}$. The peaks around 1290 $cm^{-1}$ are ascribed to aromatic amine. It moved to 1234 $cm^{-1}$ and 1242 $cm^{-1}$ in polyaniline/*Alastonia scholaris* and polyaniline/*Polyalthia longifolia* composites respectively, because of doping. The bands in the range of 1121 $cm^{-1}$ are characteristic of conductive polyaniline. These are considered to be a measure of degree of electron delocalization. This characteristic band shifts from 1236 $cm^{-1}$ in polyaniline to 1161 and 1153 $cm^{-1}$ in polyaniline/*Alastonia scholaris* and polyaniline/*Polyalthia longifolia* composites respectively[39,40].

## Adsorption studies

**Effect of adsorbent dose:** The effect of variation in adsorbent dose on the percentage removal of Ni(II) and Cu(II) was studied using two adsorbents *i.e.* polyaniline/*Alastonia scholaris* and polyaniline/*Polyalthia longifolia*. The results are presented in Figs. 6 and 7. It was observed that the percentage removal of Ni(II) increased with increasing adsorbent dose of polyaniline/*Alastonia scholaris* but decreased in case of polyaniline/*Polyalthia longifolia*, while in case of Cu(II) ions, it is increased with both adsorbents. The maximum % age removal values for Ni(II) were obtained when polyaniline/*Alastonia scholaris* dose was 0.7 g with 55.348 % removal, while with polyaniline/*Polyalthia longifolia* it was at 0.1 g with 53.156 % adsorption. In case of Cu(II), optimum adsorption occurred at 0.7 g with 30.32 % maximum removal using polyaniline/*Alastonia scholaris* and at 0.5 g with 11.18 % maximum removal polyaniline/*Polyalthia longifolia*. After maximum adsorption of metal ions, % age adsorption rate decreases due to coagulation of adsorbent particles, which make adsorption sites less available for binding[19].

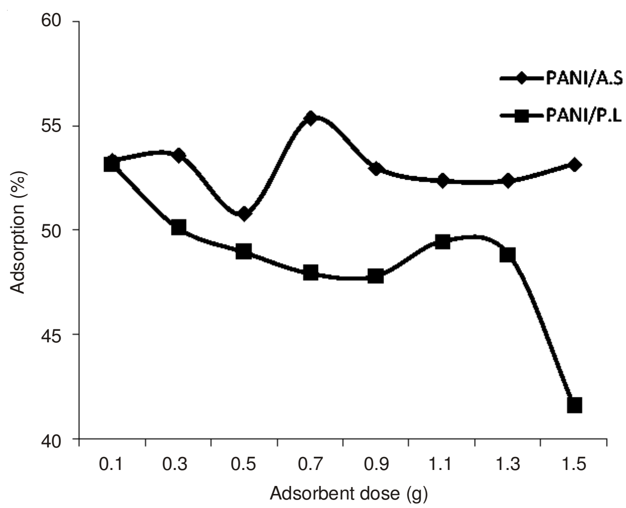


Fig. 6. Comparative graph showing effect of adsorbent dosage on % age adsorption of Ni(II) by Polyaniline composites with *Alastonia scholaris* (PANI/A.S) and *Polyalthia longifolia* (PANIA/P.L) leaves

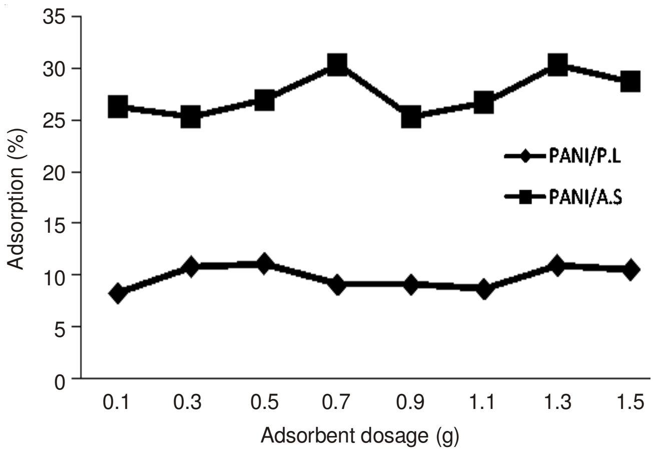


Fig. 7. Comparative graph showing effect of adsorbent dosage on % age adsorption of Cu(II)by Polyaniline composites with *Alastonia scholaris* (PANI/A.S) and *Polyalthia longifolia* (PANIA/P.L) leaves

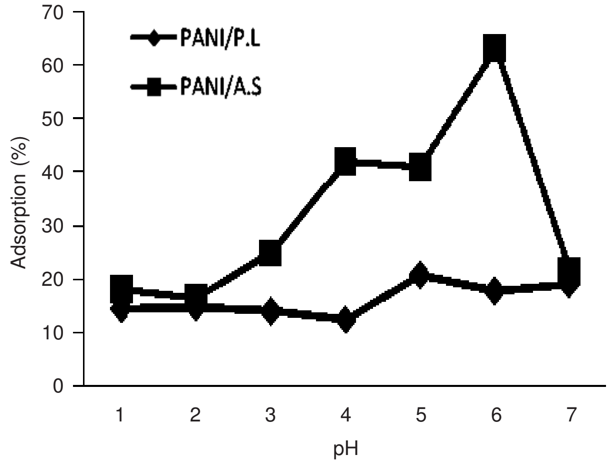


Fig. 9. Comparative graph showing effect of pH on % age adsorption of Cu(II) by Polyaniline composites with *Alastonia scholaris* (PANI/A.S) and *Polyalthia longifolia* (PANIA/P.L) leaves

**Effect of pH:** The pH of adsorbate solution affects adsorption process. The % age removal of Ni(II) and Cu(II) was studied as a function of pH in range of 1-7. Alkaline pH was avoided because it results in the precipitation of $Ni(OH)_2$ and $Cu(OH)_2$.[20] The results are shown in Figs. 8 and 9. The maximum adsorption of Ni(II) was observed at pH 5 with polyaniline/*Alastonia scholaris* with 58.308 % removal and in case of polyaniline/*Polyalthia longifolia* it was at pH 6 with 82.60 % removal. In case of Cu(II) maximum adsorption was at pH 6, using polyaniline/*Alastonia scholaris* and at pH 5 using polyaniline/*Polyalthia longifolia* with maximum removal of 63.20 % and 20.56 %, respectively. The lower adsorption capacity in severely acidic conditions is because of greater concentration of proton ($H^+$) in aqueous medium that compete with Cu(II)/Ni(II) ions for the adsorption sites of composites. By increasing pH, the $H^+$ ions concentration dropped down leading to increased metal ion uptake, because number of competing protons reduced due to neutralization. So in nearly basic to neutral condition, better adsorption takes place[42-44]. This effect of pH also pointed out the fact that chemisorptive mode of adsorption is more dominant over physio-sorption. That is further confirmed in isothermal studies.

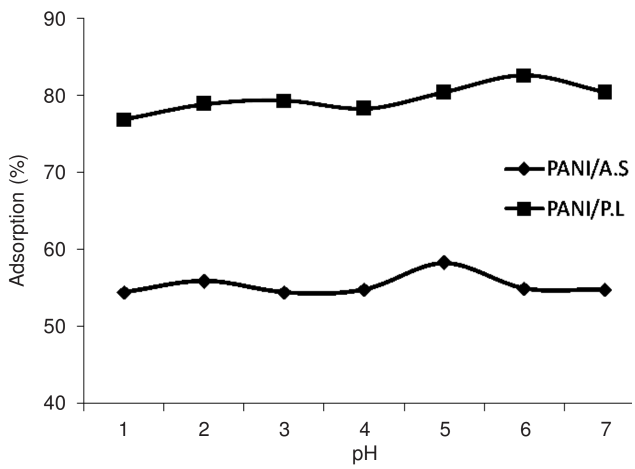


Fig. 8. Comparative graph showing effect of pH on % age adsorption of Ni(II) by polyaniline composites with *Alastonia scholaris* (PANI/A.S) and *Polyalthia longifolia* (PANIA/P.L) leaves

**Effect of temperature:** The adsorption of Ni(II) and Cu(II) on polyaniline/*Alastonia scholaris* and polyaniline/*Polyalthia longifolia* were studied at various temperatures ranging 20-70 ºC. The results are given in Figs. 10 and 11. The maximum adsorption of Ni(II) was observed at 20 ºC with polyaniline/*Alastonia scholaris* with 56.264 % removal and in case of polyaniline/*Polyalthia longifolia* it was at 30 ºC with 80.63 % removal. Adsorption is usually an exothermic process, so at relatively higher temperatures, less adsorption of metal ions occurred. In case of Cu(II) maximum adsorption was at 40 ºC using polyaniline/*Alastonia scholaris* and at 30 ºC using polyaniline/*Polyalthia longifolia* with maximum removal of 24.12 % and 16.54 % respectively. Decrease in adsorption is related with the fact that at elevated temperature, water molecules move with more speed and less time of interaction was available for adsorbate with adsorbent active sites. Secondly adsorption is generally an exothermic process, so at higher temperature, the efficiency of process decreases. That is further confirmed by thermodynamical modelling of equilibrium data of adsorption[45].

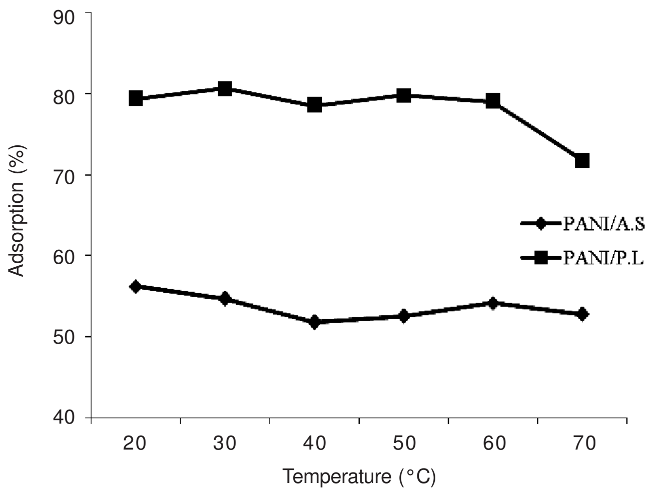


Fig. 10. Comparative graph showing effect of temperature on % age adsorption of Ni(II) by Polyaniline composites with *Alastonia scholaris* (PANI/A.S) and *Polyalthia longifolia* (PANIA/P.L) leaves

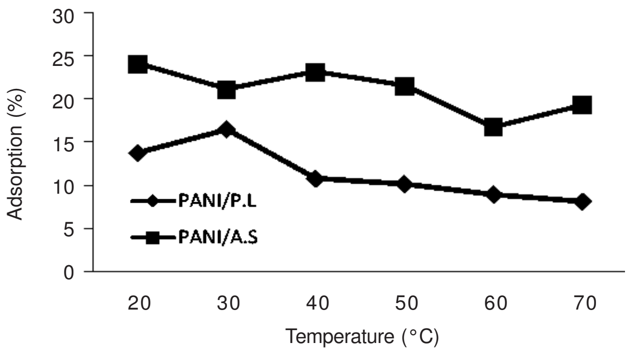


Fig. 11. Comparative graph showing effect of temperature on % age adsorption of Cu(II)by Polyaniline composites with *Alastonia scholaris* (PANI/A.S) and *Polyalthia longifolia* (PANIA/P.L) leaves

**Effect of contact time:** The adsorption phenomena is a time dependant process. The effect of various time intervals on the % age removal of Ni(II) and Cu(II) using polyaniline/*Alastonia scholaris* and polyaniline/*Polyalthia longifolia* were studied. The results are presented in Figs. 12 and 13. The maximum adsorption of Ni(II) in case of polyaniline/*Alastonia scholaris* was observed at 15 min with 55.79 % removal and using polyaniline/*Polyalthia longifolia* it was at 30 min with 59.16 % removal. Whereas in case of Cu(II), maximum adsorption was found at 50 min using polyaniline/*Alastonia scholaris* and at 45 min using polyaniline/*Polyalthia longifolia* with maximum removal of 28.92 % and 17.16 % respectively. At initial stage more binding sites were available for chelation of metal ions, but after establishing equilibrium, further chemisorptive removal of metal ions hindered away because of lack of binding sites. Slower intra-particle diffusion of metal ions into heteroge neously distributed binding sites in deeper layers of polyaniline composites is indicated by decline in adsorption as indicated from respective Figs. 12 and 13. This reduction in adsorption of metal ions with elapse of time was due to the fact that mass transfer between solution and adsorbents decreases because all available binding sites are already occupied[22,39].

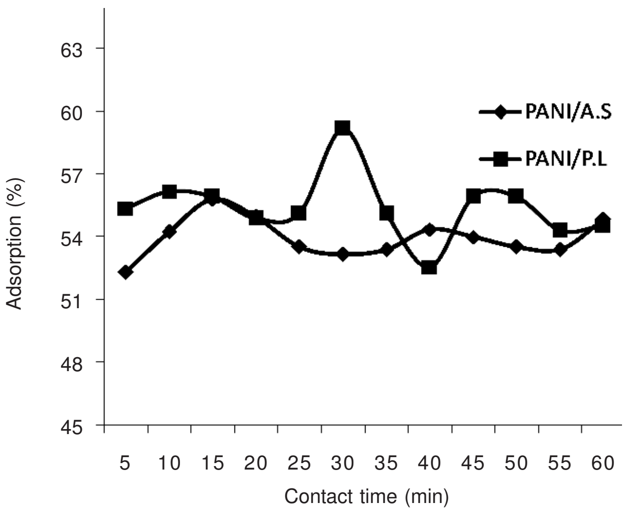


Fig. 12. Comparative graph showing effect of contact time on % age adsorption of Ni(II) by Polyaniline composites with *Alastonia scholaris* (PANI/A.S) and *Polyalthia longifolia* (PANIA/P.L) leaves

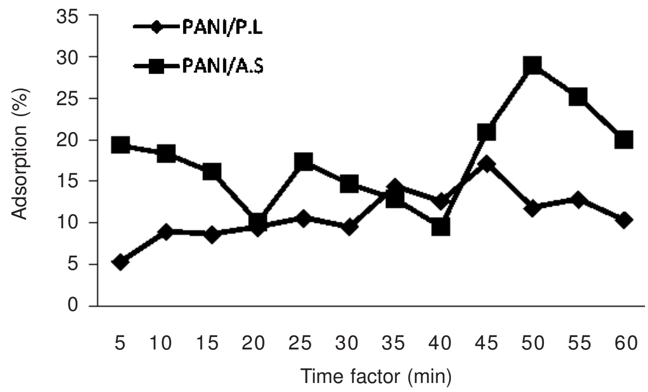


Fig. 13. Comparative graph showing effect of contact time on % age adsorption of Cu(II) by Polyaniline composites with *Alastonia scholaris* (PANI/A.S) and *Polyalthia longifolia* (PANIA/P.L) leaves

**Mechanism of adsorption in terms of isothermal studies:** Optimized conditions of adsorption for removal of Ni(II) and Cu(II) by polyaniline/*Polyalthia longifolia* and polyaniline/*Alastonia scholaris* were applied simultaneously to 30-70 ppm metal ion concentration for studying adsorption isotherm. Langmuir isotherm was plotted using eqn. 4:

$$\frac{1}{q} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \quad (4)$$

Here q (mg/g) is the amount of metal ions adsorbed by composites, $C_e$ (ppm) is the remaining concentration of metal ions after adsorption experiment, $q_m$ (mg/g) and b (L/g) are Langmuir isotherm constants calculated from regression analysis of the linear plots of 1/q *versus* $1/C_e$. The value of q is calculated by using eqn. 5:

$$q = \frac{(C_o - C_e)V}{m} \quad (5)$$

whereas 'V' is the volume of metal ions solution in liters and m is the mass of composites used in grams. Freundlich isotherm was drawn eqn. 6:

$$\log q = \log K_F + \frac{1}{n}\log C_e \quad (6)$$

In this equation, $K_F$ and n are Freundlich isotherm parameters, whose values were calculated[39-41] from slope and intercept of graph of log q *versus* log $C_e$. The corresponding parameters of Langmuir model are given in Table-4 and of Freundlich in Table-5. The correlation ($R^2$) values of Freundlich model followed more than Langmuir in case of polyaniline/*Alastonia scholaris* for both Ni(II) and Cu(II) adsorption, whereas Langmuir model followed more than Freundlich in case of polyaniline/*Polyalthia longifolia* for both Ni(II) and Cu(II) adsorption.

Langmuir model applicability indicated that mono layer chemisorptive removal of metal ions occurred more on composite, whereas Freundlich model applicability indicated that binding sites are heterogeneously distributed in these composites which facilitates physio-sorptive removal of metal ions. Fig. 14 is showing the mechanism of chemisorptive removal of Cu (II) and Ni (II) by polyaniline/*Polyalthia longifolia* and polyaniline/*Alastonia scholaris* composites. Amino groups in polyaniline are used for chelating metal ions, whereas leaf

TABLE-4
LANGMUIR ISOTHERMAL PARAMETERS FOR ADSORPTION OF Cu(II) AND Ni(II) BY POLYANILINE COMPOSITES WITH *Alastonia scholaris* (PANI/A.S) AND *Polyalthia longifolia* (PANI/P.L) LEAVES

| Metal ion | Adsorbent | Slope | Intercept | $R^2$ | $q_m$ (mg/g) | b (L/g) | $\Delta G^o$ (kJ/mol) |
|---|---|---|---|---|---|---|---|
| Ni(II) | PANI/A.S | 3.294 | 0.062 | 0.989 | 16.17 | 0.019 | -9.819 |
| | PANI/P.L | 0.005 | 0.086 | 0.890 | 11.64 | 17.18 | -7.046 |
| Cu(II) | PANI/A.S | 0.040 | 0.032 | 0.968 | 31.25 | 0.800 | -0.553 |
| | PANI/P.L | 2.135 | 0.035 | 0.907 | 28.21 | 0.017 | -10.095 |

TABLE-5
FREUNDLICH ISOTHERMAL PARAMETERS FOR ADSORPTION OF Cu(II) AND Ni(II) BY POLYANILINE COMPOSITES WITH *Alastonia scholaris* (PANI/A.S) AND *Polyalthia longifolia* (PANIA/P.L) LEAVES

| Metal ion | Adsorbent | Slope | Intercept | $R^2$ | n | $K_F$ ($mg^{1-1/n}$ $L^{1/n}$ $g^{-1}$) |
|---|---|---|---|---|---|---|
| Ni(II) | PANI/A.S | 0.688 | -0.259 | 0.986 | 1.452 | 0.550 |
| | PANI/P.L | 0.612 | 0.063 | 0.861 | 1.16 | 1.634 |
| Cu(II) | PANI/A.S | 0.552 | 1.109 | 0.920 | 12.853 | 1.812 |
| | PANI/P.L | 0.612 | 0.063 | 0.861 | 1.16 | 1.634 |

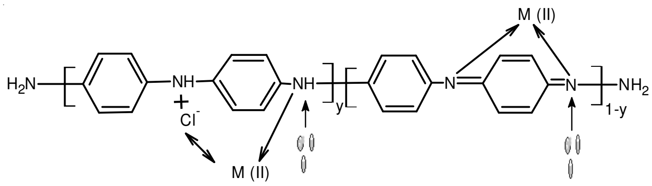


Fig. 14. Mechanism for metal ions removal by polyaniline composites with *Alastonia scholaris* (PANI/A.S) and *Polyalthia longifolia* (PANI/P.L) leaves. Where M(II) = Cu(II)/Ni(II)

powder enhances the polyaniline structure heterogeneity, exposing more chelating sites. It also helps in improving physiosorptive removal of these metal ions as shown by applicability of Freundlich model[42-46]. The maximum adsorption capacities of polyaniline/*Alastonia scholaris* composites for removing Ni(II) and Cu(II) are: 16.17 and 31.25 mg/g respectively, while in case of polyaniline/*Polyalthia longifolia* composites for removing Ni(II) and Cu(II) are: 11.64 and 28.21 mg/g respectively. These values are comparable to already reported literature for adsorption of Ni(II) and Cu(II) to a great extent, as evident from Table-6, which suggested the suitability of these novel adsorbents[17-37]. Whereas physiosorption Freundlich constant 'n' value was more in case of polyaniline/*Alastonia scholaris* composites as compared to polyaniline/*Polyalthia longifolia* composites for both metal ions, showing that *Alstonia scholaris* leaf powder modify polyaniline surface area more as compared to *Polyalthia longifolia* leaf powder during composite formation[47], which enhances their maximum adsorption capacity values more as evident from Tables 4 and 5.

TABLE-6
COMPARISON OF MAXIMUM ADSORPTION CAPACITY OF PANI COMPOSITES FOR REMOVING Ni(II) AND Cu(II) WITH ALREADY REPORTED ADSORBENTS

| Ni (II) | | Cu(II) | |
|---|---|---|---|
| Adsorbent | $q_m$ (mg/g) | Adsorbent | $q_m$ (mg/g) |
| Bagasse fly ash | 6.49 | Saw dust | 6.58 |
| Coir pith | 15.95 | Peanut hulls | 8.37 |
| Black carrot residues | 6.51 | Sago waste biomass | 12.4 |
| Waste pomace of olive oil factory | 14.80 | *Sargassumfluitans* | 10.37 |
| pomegranate peel | 52 | Tobacco dust | 36 |
| Wheat unmodified | 2.29 | Pomegranate peel | 1.32 |
| Barley straw | 35.8 | Sugar beet pulp | 31.4 |
| Oat unmodified | 3.04 | Chestnut shell | 12.56 |
| sugarcane bagasse | 2.0 | Apple wastes | 10.8 |
| PANI/A.S | 16.17 | PANI/A.S | 31.25 |
| PANI/P.L | 11.64 | PANI/P.L | 28.21 |

**Thermodynamical investigations:** Thermodynamic parameter $\Delta G^o$ (Gibbs free energy change) is determined from equilibrium data using Langmuir isotherm constant 'b' by eqn. 7 as described in our earlier work:[39,40]

$$\Delta G^o = - RT \ln(K) \quad (7)$$

As it is obvious from Table-5 that removal of Ni(II) and Cu(II) with polyaniline/*Alastonia scholaris* composites is more favourable as compared to polyaniline/*Polyalthia longifolia* composites because of larger $\Delta G^o$ values. This fact is also su pported by their large '$q_m$' values.

**Regeneration of adsorbent:** The regeneration of used adsorbents using different acids was quantified and the results are shown in Fig. 15. It was found that as compared to

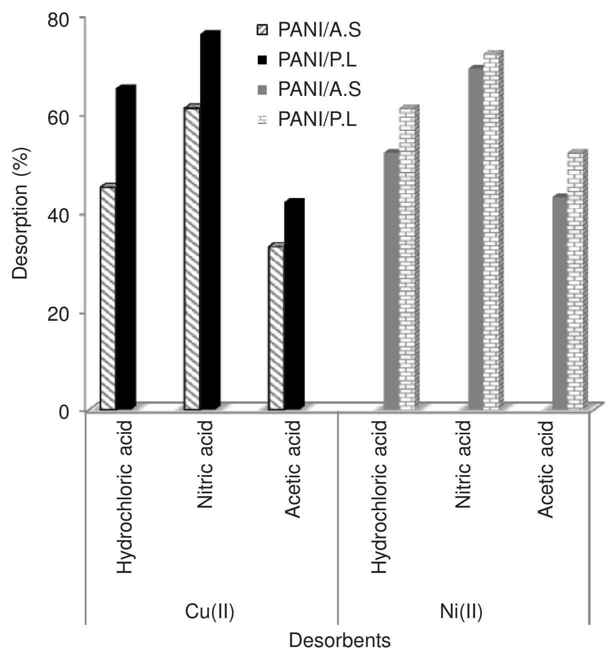


Fig. 15. Comparative graph showing effect of different eluents on % age desorption of Cu(II) and Ni(II) by polyaniline composites with *Alastonia scholaris* (PANI/A.S) and *Polyalthia longifolia* (PANIA/P.L) leaves

other acids, $HNO_3$ is a good eluent for desorption of Cu(II) and Ni(II) from polyaniline/*Alastonia scholaris* and polyaniline/*Polyalthia longifolia* composites, because solubility of nitrates of these metal ions are more as compared to other salts. The regenerated adsorbent can be reused in adsorption processes after washing and drying[40].

## Conclusion

It can be safely concluded that polyaniline composites with agro-waste materials like *Polyalthia longifolia* and *Alstonia scholaris* leaves can be efficiently employed for metal ion removal from waste-water. Optimized conditions for the removal of Ni (II) using polyaniline/*Alastonia scholaris* composite were as followed: adsorbent dose 0.7 g, pH 5, temperature 20 and contact time 15 min. While using polyaniline/*Polyalthia longifolia* composite these conditions were found optimized for removal of Ni(II): adsorbent dose 0.1 g, pH 6, temperature 30 ºC and contact time 30 min. For Cu(II) optimized conditions using polyaniline/*Alastonia scholaris* composite were as followed: adsorbent dose 0.7 g, pH = 6, temperature 40 ºC and contact time 50 min. Whereas with polyaniline/*Polyalthia longifolia* composite, these conditions were: adsorbent dose 0.5 g, pH 5, temperature 30 °C and contact time 45 min.The porosity of polyaniline polymer increases by making its composites with leaf powder. Results indicated that polyaniline/*Alastonia scholaris* composites are more efficient in adsorbing Ni(II) and Cu(II) as compared to polyaniline/*Polyalthia longifolia* composites as indicated from their maximum adsorption capacity values. Both chemisorption and physiosorption mode are involved for adsorption of these metal ions from water. Using dilute nitric acid solution, polyaniline/*Alastonia scholaris* and polyaniline/*Polyalthia longifolia* composites can be regenerated after adsorption.

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