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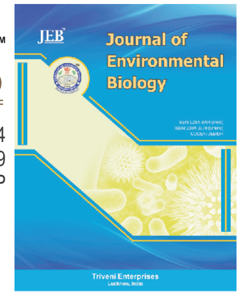

Defluoridation of water with the help of copper phytoremediated *Andrographis paniculata* plant biomass

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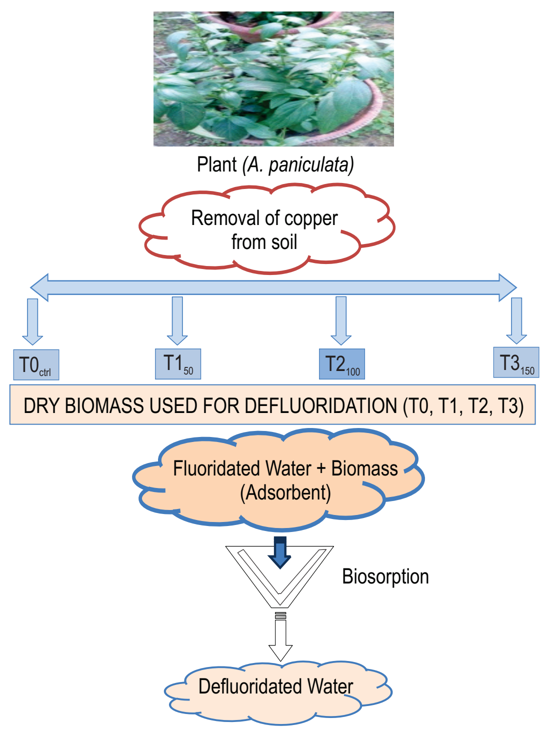
Abstract

Aim : The present study aimed to defluoridate water with the help of copper phytoremediated *A. paniculata* plant biomass.

Methodology : One gram of dry root and shoot of *A. paniculata* (30, 60 and 90 days) grown in Cu treated soil (50, 100, 150 mg kg^{-1}) was digested separately in a solution of HNO_3:$HClO_4$ (3:1) at 70–80°C and was subsequently analyzed on atomic absorption spectrophotometer (AA 240 FS, Varian). Biomass of fresh shoot of *A. paniculata* 90 days after sowing (DAS) were collected from the experimental pots (T0, T1, T2 and T3) and washed carefully with double distilled deionized water and sun dried till constant weight. Dried plant biomass samples were ground manually and sieved to obtain powder of below 1.5 mm diameter and used as a biosorbent. Before applying as a biosorbent, the obtained powdered sample was subjected to acid/alkali treatment. The treated plant material was washed repetitively with double distilled water till clear solution having pH 7 was obtained.



Results : Cu accumulation in roots and shoots after 30, 60 and 90 DAS ranged between 38.19-70.70, 57.23-97.38 and 73.47-184.24 and 25.41-51.23, 26.71-55.75 and 43.16-118.03 µg g^{-1} d.wt. respectively. Enrichment coefficient of Cu in root (EC_{root}) and shoots (EC_{shoot}) at 30, 60 and 90 days after treatment ranged between 0.47-0.92, 0.65-1.14, 1.23-2.60 and 0.34-0.51, 0.37-0.53, 0.67-1.48 respectively. The dried and ground biomass of *A. paniculata* had successfully reduced fluoride concentration in water from 5 to 0.784 (mg l^{-1}) accounting for 84% removal at an adsorbent dose of 1.5 mg, contact time 100 min. and pH 3, respectively.

Interpretation : The correlation coefficient (R^2) confirmed the suitability of Langmuir and Freundlich isotherms. The R_L values indicated favorable adsorption process. Furthermore, Freundlich constant (n) was found to be greater than 1 which also confirmed the favorable adsorption process.

Introduction

Rampant industrialization and unorganized anthropogenic activities throughout the world has laid increasing pressure on all components of the environment by releasing enormous quantities of organic as well inorganic contaminants including metal and metalloids. Soil contamination with metals due to several anthropogenic deeds like improper waste management practices, landfill operations, mining, manufacturing and application of sewage sludge etc. has emerged as a major environmental challenge. Agricultural field contamination with metals is not only degrading the quality of soil and foods,but also poses a threat to human health and ecosystem (Mapanda *et al.,* 2005; Singh *et al.,* 2010). Bioavailability of copper (Cu) in soil at optimum concentration is considered as essential micronutrient because it play an important role in plant growth and development (Yruela, 2009), however, its bioavailability even at slightly higher than the optimal level can cause phytotoxicity (Michaud *et al.,* 2008). Anthropogenic deeds e.g. use of pesticide, fungicides and Cu-rich slurries during agricultural practices elevates the level of Cu in soil (Legros *et al.,* 2010; Nagajyoti *et al.,* 2010). Higher concentration of Cu in soil interferes with the availability of various nutrients by converting ionic species to non-ionic form. At elevated concentration, Cu can hamper the plant growth by enhancing the generation of reactive oxygen species (ROS) like hydrogen peroxide (H_2O_2) (Adrees *et al.,* 2015; Habiba *et al.,* 2015; Mei *et al.,* 2015). Various *in situ* and *ex situ* remediation approaches like stabilization, solidification, soil washing, vitrification, electrokinetic treatment and phytoremediation are being used for the restoration of metal contaminated land. Among these techniques phytoremediation is a technique that utilizes living plants to reduce, remove, degrade or immobilize the contaminants. This technique emerges as an economical, eco-friendly and most aesthetically acceptable technique (Kumar *et al.,* 2012; Stingu *et al.,* 2012; Kumar *et al.,* 2013; Chayapan *et al.,* 2015). However, proper utilization of biomass generated after phytoremediation is an important concern.

Globally, more than 200 million people are affected with fluorosis in more than twenty nine countries including India (Ayoob *et al.,* 2008). Several techniques are available for the removal of fluoride from water *viz.,* precipitation (Reardon and Wang, 2000), ion exchange, reverse osmosis (Ndiayea *et al.,* 2005), electrodialysis (Kabay *et al.,* 2008) and adsorption (Karthikeyan *et al.,* 2009; Mohan *et al.,* 2012a). Among the available techniques, adsorption had been proven to be effective and economical. Various adsorbents like aluminum based material (Ayoob *et al.,* 2008), algal biosorbent (Mohan et al., 2007), chitosan beads (Liu *et al.,* 2014; Miretzky and Cirelli, 2011), clay soil, carbon based material (Eric *et al.,* 2010; Mohan et al., 2012b), powdered *Tinospora cordifolia* (Pandey *et al.,* 2012), *Echhornia crassipes* (Sinha *et al.,* 2003), lime (Islam and Patel, 2006; Gogoi *et al.,* 2015), wheat straw dust, saw dust raw and activated biogass carbon (Yadav *et al.,* 2013) etc. have been applied for the defluoridation. In view of the above, the present study was carried out to assess defluoridation of water with the help of copper phytoremediated *Andrographis paniculata* plant biomass.

Materials and Methods

Phytoremediation of Cu; plant materials and treatments : Certified seeds of *Andrographis paniculata* were procured from the National Seed Disposal Centre, Lucknow, Uttar Pradesh, India. Seed were sown in 30 cm-diameter earthen pots filled with 8.5 Kg (approx) soil. All the pots were watered regularly with ground water to keep the soil moist. Nitrogen (N), phosphorus (P) and potassium (K) @120, 30 and 80 mg kg^{-1} soil respectively were applied at the time of sowing in the form of urea, single super phosphate and potash. Soil treatments of Cu were prepared by mixing the appropriate amount of $CuSO_4$ to achieve 50, 100 and 150 mg Cu kg^{-1} soil along with control *i.e.,* garden soil. The pots sowed with the seed of *A. paniculata* were kept in the net house of research field station of the Department of Environmental Science, Babasaheb Bhimrao Ambedkar University, Lucknow, India. Seed germination was recorded after six days of sowing and thereafter, plants were thinned to three plants per each pot for further studies. To determine the metal accumulation potential one plant from each pot was uprooted at the interval of 30, 60 and 90 days after sowing (DAS). Physico-chemical parameters of experimental soil were examined before initiating the pot experiment.

Estimation of metal content, Enrichment coefficient and Translocation factor : One gram of dried plant sample was digested in a solution of HNO_3: $HClO_4$ (3:1) at 70–80°C for metal estimation. The solution was allowed to evaporate by raising the temperature to 105°C until the solution becomes transparent. The final volume was diluted to 25 ml with 0.1 N HNO_3, filtered through Whatman no. 42 filter paper and analyzed on atomic absorption spectrophotometer (AA 240 FS, Varian) (Piper, 1942).

Enrichment coefficient (EC) has been determined to derive the degree of heavy metal accumulation in plants following Kisku *et al.* (2000). Translocation factor (TF) or mobilization ratio of each metal was calculated to determine the translocation of metals from root to shoot of the plant species following Barman *et al.* (2000).

Defluoridation of water : A 100 mg l^{-1} stock solution of fluoride was prepared by dissolving 221 mg of anhydrous sodium fluoride of 99.5% purity in one liter of distilled deionized water from Millipore. Test concentration of 5 mg l^{-1} was prepared from stock solution following serial dilution technique. Test concentration of 5 mg l^{-1} was selected for adsorption experiment since it is considered to be normal fluoride concentration in groundwater. Fresh shoot of *A. paniculata* of 90 days age were collected from the experimental pots (T0, T1, T2 and T3) used for phytoremediation of Cu from the soil. Plant parts were washed carefully with double distilled deionized water and sun dried for 3 days. Dried plant biomass samples were ground manually with the help of mortar pestle and sieved to obtain powder of below 1.5 mm diameter. Before applying as biosorbent; the obtained powdered sample was subjected to acid/alkali treatment. Powdered sample of *A. paniculata* (50 gm) was mixed with 500 ml of 1 M HNO_3 and heated gently for 20 min. on open flame burner then filtered out and washed with double distilled water till the elimination of color. Acid treated sample was subsequently subjected to alkali treatment with 500 ml of 0.5 M NaOH. The treated plant material was washed repetitively with double distilled water till a clear solution of pH 7 was obtained. The obtained powdered biomass was oven dried for 3 hrs at 110°C and subsequently cooled in air to room temperature for use.

Results and Discussion

Physico-chemical properties of experimental soil were investigated prior to seed sowing. Soil was found slightly alkaline with pH 7.41, EC 0.46 ds m^{-1} and organic carbon 1.38%. Soil was found to be rich in Ca : 3.02 ppm; Fe : 114.32 ppm; Mn: 7.2 ppm; Na: 3.17 ppm; S: 16.58 ppm; and Zn: 2.73ppm. N, P and K content of the soil was found to be 1.39, 0.94 and 3.52 g kg^{-1}, respectively. Ni, Pb, Cu and Cr were present in traces.

Accumulation of Cu in roots of *A. paniculata* was higher than the shoots in all treatments. Cu accumulation in roots and shoots after 30, 60 and 90 DAS ranged between 38.19-70.70, 57.23-97.38 & 73.47-184.24; 25.41-51.23, 26.71-55.75 and 43.16-118.03 μg g^{-1} d.wt., respectively (Table 1). Enrichment coefficient (EC) was used to determine the degree of metal accumulation in roots and shoots with respect to metal concentration in growing medium. EC_{root} is used as an index for the transfer of metal from soil to plant root, while EC_{shoot} determines the degree of transfer of metal from soil to shoot. EC also represents a special feature of the plant to absorb the metals from soil, and subsequently transport them to aerial parts (Zhao *et al.,* 2003; Chen *et al.,* 2005). EC_{root} and EC_{shoot} for Cu at 30, 60, 90 days after treatment ranged between 0.47-0.92, 0.65-1.14, 1.23-2.60 and 0.34-0.51, 0.37-0.53, 0.67-1.48, respectively (Fig. 1). A higher value of EC_{root} as compared to EC_{shoot} indicates that largely the metal was retained in roots.

It has been reported that EC>1 indicates the potential of plants to extract and transport metals from the substrate to different plant parts (Wei *et al.,* 2002). Such plant species are considered as hyperaccumulator and can be applied for phytoextraction of metals (Barman *et al.,* 2000; Kumar *et al.,* 2013). Translocation factor (TF) or mobilization ratio determines the translocation of metals from root to shoot and can be used to assess the potential of a plant for phytoremediation. TF for Cu, at 30, 60 and 90 days after treatment ranged between 0.42-0.72, 0.44-0.58 and 0.53-0.64, respectively. The results revealed that the metal was moderately translocated from root to shoot in *A. paniculata* (Fig. 1). Several batch experiment were performed to study the adsorption of flouride using *A. paniculata* leaves as biosorbent under different conditions. It was found that the adsorption capacity of biosorbent (powdered leaf sample) was influenced by contact time, pH, initial F concentration and adsorbent dose.

The influence of contact time on the adsorption efficiency of F was studied by varrying the contact time from 20 to 120 min. at the adsorbent dose of 5 g per 25 ml, pH 3 and temparature 28±2°C. It was found that initially, the fluoride removal efficieny increased with increase in contact time, however, after 100 min. it became almost stagnant denoting the attainment of adsorption saturation (Fig. 2a). Rapid adsorption at the initial stage may be due to availability of enough active sites for fluoride adsorption, however, with the progress of experiment the active sites became saturated and ultimately, the adsorbent might have been exhausted at the final stages (Killedar and Bhargava, 1993; Chen *et al.* 2015; Kumari and Khan, 2017; Kofa *et al.* 2017). Similar findings were reported with various other bisorbents; *Pleurotus ostreatus* 1804 (Ramanaiah *et al.,* 2007), protonated chitosan beads (Viswanathan *et al.,* 2009), *Citrus limonum* leaf (Tomar *et al.,* 2014), wheat straw, sawdust and activated bagasse (Yadav *et al.,* 2013).

It is an established fact that the process of biosorption is reliant on the pH, functional groups of the biosorbent and their ionic state (Liu *et al.,* 2014; Yadav *et al.,* 2013). Fluoride removal efficiency was found to decrease with increased pH (Fig. 2b). Biosorbent contains a high amount of polysaccharides and some of them are associated with protiens and other biomolecules (Williams and Edyvean, 1997; Panumati *et al.,* 2008). These biomolecules have several functional groups e.g., amine, carboxyl, thiol, sulfhydryl, alcohol, phenol and phosphate. The phenomenon of biosorption depends on the protonation or deprotonation of these functional groups (Ilhami *et al.,* 2005). The ionic form of fluoride in aqueous solution and the electric charge of the functional groups of biomolecules (the surface biosorbent) depends on the pH of the solution. Further, at higher pH, the adsorbent surface becomes negatively charged which leads to electrostatic repulsion between fluoride and

Table 1 : Accumulation of Cu (μg g^{-1} d.wt.) in different plant parts of *A. paniculata* after 30, 60 and 90 days of sowing (DAS)

Sample	30 DAS		60 DAS		90 DAS	
	Root	Shoot	Root	Shoot	Root	Shoot
T0	5.81±0.023[a]	2.47±0.005[a]	6.91±0.32[a]	2.83±0.06[a]	16.37±0.56[a]	9.31±0.56[a]
T1	38.19±1.05[b]	25.41±0.93[b]	57.23±1.09[b]	26.71±1.02[b]	73.47±6.2[b]	43.16±2.92[b]
T2	53.75±1.12[c]	38.48±1.43[c]	76.06±2.41[c]	44.07±1.13[c]	125.51±7.01[c]	66.87±3.12[c]
T3	70.70±2.82[d]	51.23±2.03[d]	97.38±4.08[d]	55.75±2.17[d]	184.24±7.42[d]	118.03±6.64[d]

Values represent mean of five replicates ± SE; Different letters indicates that means are significantly different from each other (p<0.05) adsorbent surface resulting in low adsorption capacity (Gajbhiye *et al.,* 2017; Kumari and Khan, 2017).

The effect of adsorbent dose on the fluoride removal from water was examined at pH 6 and contact time of 80 min. The amount of dosage were varied between 0.5 gm to 3 gm per 25 ml. The results revealed that upto a certain level, an increase in adsorbent dose resulted in a simultaneous increase in F removal, probably due to high availibity of surface area and pore volume. Flouride removal efficiency increased from 45.4, 50.8, 49.8 and 51.4 to 79.2, 82.14, 82.8 and 83.6%, respectively at 0.5-3 gm dose in different treatments (Fig. 2 c). All the treatments have followed the similar fluoride removal trend, however, over 1.5 gm adsorbent doses, there were no significant changes in the fluoride removal was noticed; the reason being the overlapping of active sites at a higher dosage, thus decrease in the net available surface area for adsorption (Killender and Bhargava, 1993; Mondal *et al.,* 2016). Similar results were reported with various other bisorbents *viz.* protonated chitosan beads (Viswanathan *et al.,* 2009), *Citrus limonum* leaf (Tomar *et al.,* 2014), *Azadirachta indica* (Chakrabarthy and Sharma, 2012), wheat straw, sawdust and activated bagasse (Yadav *et al.,* 2013).

The effect of initial fluoride concentration on the removal efficiency was investigated by adding the fixed amount of adsorbent dose (2 gm) into different concentrations of fluoride solution (2.5, 5, 7.5, 10, 12.5 and 15 mg l^{-1}) for 100 min. The results demonstrated that fluoride removal efficiency decreased with increase in the initial fluoride concentration (Fig. 2d). The deacrease in fluoride removal efficiency indicates that the capacity of adsorbent gets exhausted abruptly on increasing the initial fluoride concentration probably due to instant saturation of active adsorbent sites at higher fluoride concentration (Mondal *et al.,* 2016). Similar trends have been reported by several authors

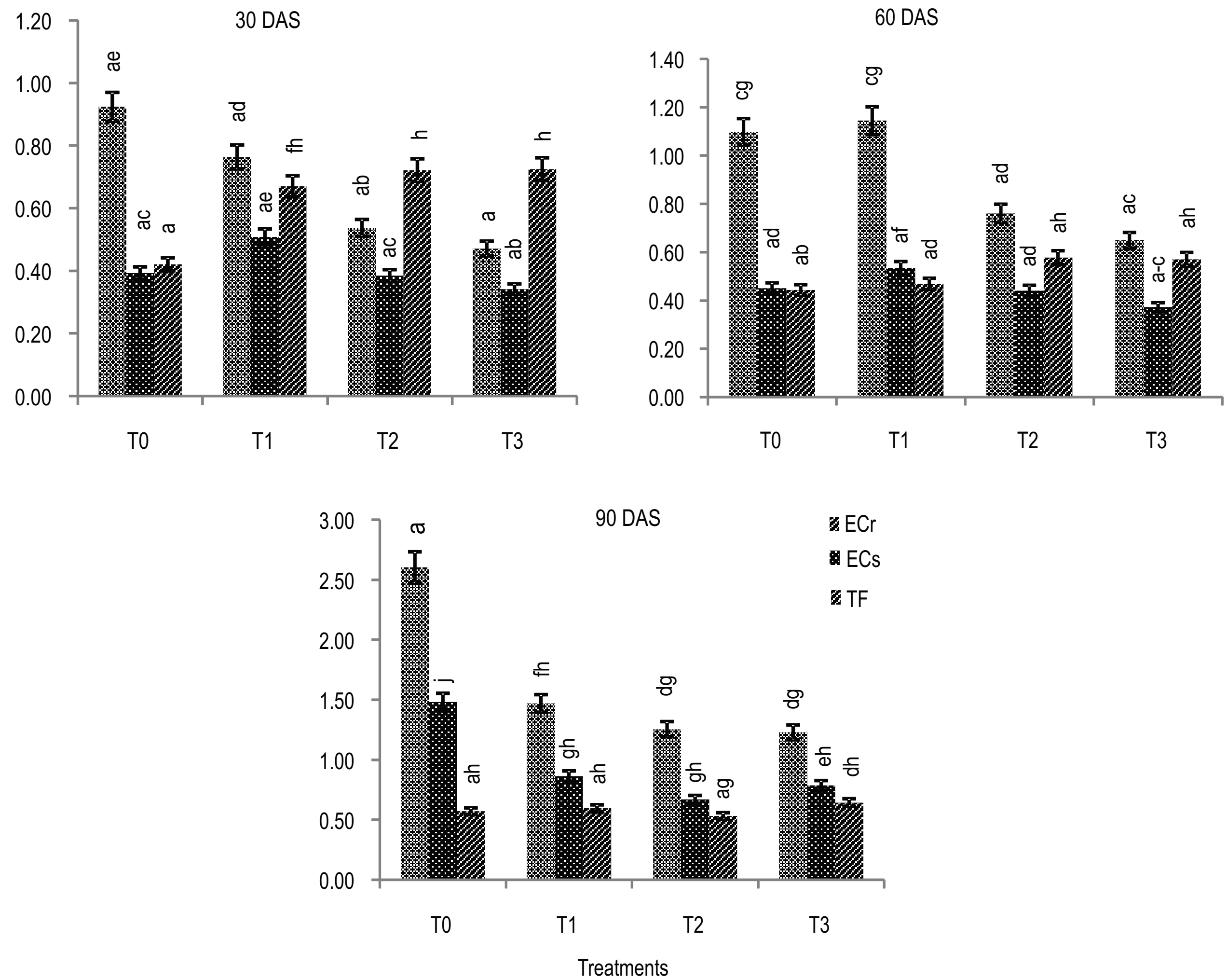


Fig. 1 : Accumulation of Cu (μg g^{-1} d.wt.) in different plant parts of *A. paniculata* after 30, 60 and 90 days of sowing (DAS). ECr- Enrichment Co efficient of root, ECs- Enrichment Coefficient of shoot, TF- Translocation Factor

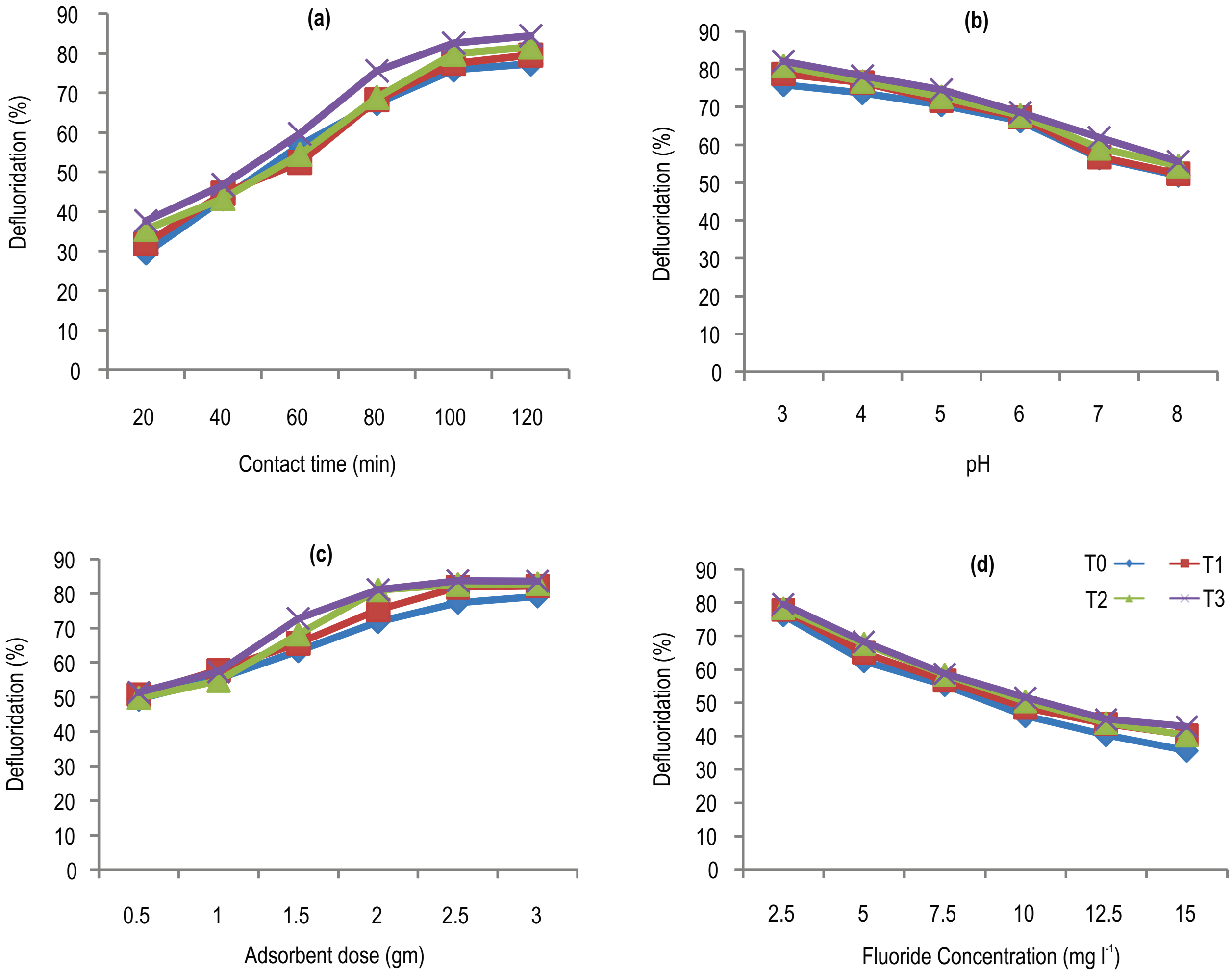


Fig. 2 : Effect of (a) contact time, (b) pH, (c) adsorbent dose and (d) initial fluoride concentration on the pecent fluoride removal from water by Cu phytoremediated *A. paniculata* plant biomass

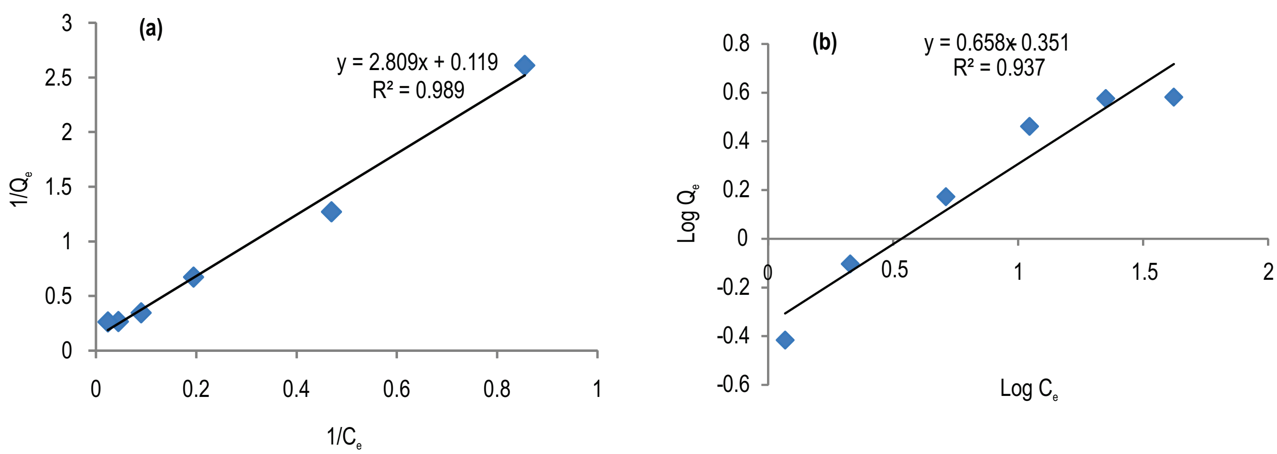


Fig. 3 : Linear model of Langmuir isotherm (a) and Freundlich isotherm (b) for adsorption of fluoride at 1g 10 ml^{-1} volume, pH 3, temp 30°C, contact time of 120 min and different initial concentration of adsorbent

for fluoride removal from water using protonated chitosan beads (Viswanathan *et al.,* 2009), algal biomass (Mohan *et al.,* 2007), wheat straw, sawdust, activated bagasse of sugarcane (Yadav *et al.,* 2013), *Azadirachta indica* (Chakrabarty and Sarma, 2012) and lemon leaf (Tomar *et al.,* 2014).

Langmuir and Freundlich isotherms are considered as essential models for understanding the adsorption process. The Langmuir isotherm is based on saturated molecular layer (monolayer) adsorption on the active sites of the adsorbate, while Freundlich isotherm is based on adsorption on a heterogeneous surface and a multilayer adsorption with an energetic non uniform distribution (Liu *et al.,* 2011; Cai *et al.,* 2015). A plot of $1/Q_e$ against $1/C_e$ shows a straight line which indicates that the adsorption process followed the Langmuir isotherm (Fig. 3a). Further, a plot of Log Q_e against Log C_e showed a linearity of Freundlich isotherm plot which confirms the applicability of Freundlich model for defluoridation at different initial concentrations (Fig. 3b).

The correlation coefficient (R^2) of Langmuir and Freundlich isotherms was greater than 0.93 indicating that both the models could explain the adsorption of fluoride. Maximum adsorption capacity (Q_{max}) from Langmuir isotherm model was 3.8 mg g^{-1} which was higher than wheat straw, sawdust, and activated bagasse (1.93, 1.73 and 1.15 mg g^{-1}) as reported by Yadav *et al.,* (2013). The values of RL ranged between of 0.118-0.681, indicating favorable adsorption process. Furthermore, Freundlich constant 'n' (n=1.51) was found to be greater than 1 which also confirms the favorable adsorption process (Zhang and Jia, 2016; Ghada *et al.,* 2018). The present study concludes that *A. paniculata* plant can be used as a moderate phytoremediator of Cu, however, use of *A. paniculata* biomass for removal of fluoride from contaminated water is an added advantage to the remediation process.

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