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Factorial design for optimizing the removal of aluminium from aqueous solutions by adsorption on *Typha domingensis* phytomass

A.K. Hegazy[a], N.T. Abdel-Ghani[b], G.A. El-Chaghaby[c]*

[a]*Department of Botany and Microbiology, College of Science, King Saud University, Riyadh, Saudi Arabia*
[b]*Chemistry Departement, Faculty of Science, Cairo University, Giza, Egypt*
[c]*Agriculture Research Center, Giza, Egypt*
Tel.: +20101235184; Email: ghadiraly@yahoo.com

ABSTRACT

Typha domingensis phytomass is used as a biosorbent for aluminium ions removal from aqueous solution. A full 2^3 factorial design of experiments is used to obtain the best conditions of biosorption of Al^{3+} from water solutions. The three factors screened are temperature, pH, and biosorbent dosage. Two levels for each factor are used; pH (2.5 and 6.0), temperature (25 and 45°C), and phytomass loading weight (0.5 and 1 g/50 ml). Batch experiments are carried out using 50 ml solutions containing 7 mg/L Al^{3+} simulating its concentration in a real wastewater effluent. Aluminium concentration in solutions is determined using ICP-OES; the removal percentages of aluminium are then evaluated. The results are analyzed statistically using the Minitab 15 statistical software to determine the most important factors affecting aluminium removal. The results revealed that pH is the most significant factor affecting aluminium ions uptake onto *Typha* phytomass.

Keywords: Biosorption; pH; Temperature; Phytomass loading weight; Biosorbent characterization

1. Introduction

The rapid development of industrialization all over the world has raised the discharge of industrial wastes, especially those containing heavy metals and trace elements, into natural water bodies or on land. Their presence in the aquatic ecosystem poses human health risks, and causes harmful effects to living organisms in water and to the consumers of them.

Aluminium (Al) is a non-essential element to which humans are frequently exposed. Aluminium is widespread throughout nature, air, water, plants and consequently in all the food [2]. Aluminium is most commonly used in food technology as cans, packaging materials, kitchen utensils, and vessels. Aluminium is also preferred due to its corrosion resistance and easy processing properties. Aluminium accumulation may increase the risks of neurological and bone diseases, e.g., Alzheimer's disease, Parkinson's disease, encephalopathy/dialysis dementia, and osteomalacia. Aluminium accumulation in the tissues of patients with chronic renal failure and monitoring of aluminium concentration in dialysis fluids has received increasing attention in the last years. The diluted dialysis fluids should not contain aluminium concentrations higher than 10 μgL^{-1} [2].

In recent years, biosorption has emerged as a cost-effective alternative for the removal of metals from aqueous solutions, using readily available biomass from nature [3]. Different biomasses have been used as metal biosorbents in many previous researches [4–7]. In these researches, many Factors were found to affect the

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*Corresponding author

Table 1
High and low levels of the screened factors

Factor	Symbol	Low level	High level
Temperature (°C)	T	25	45
Adsorbent weight (g)	X	0.5	1
pH	pH	2.5	5.5

biosorption process of heavy metals. Among these factors are temperature [8–10]; pH [11,12] initial metal concentration [11,12] and phytomass loading weight [11,12].

In the present work, the phytomass of *Typha domingensis* (Pers.) Poir.ex Steud. growing naturally in industrial wastewater ponds, Sadat city, Egypt was chosen to investigate its biosorption capacity for aluminium ions present in aqueous solution using factorial experimental design.

2 Materials and methods

2.1. Biosorbent preparation

Typha domingensis individual plants were uprooted and washed with potable water for removal of any adherent sediment, then washed with deionized water until no color was visualized in the rinse water. Plant leaves were cutted into small pieces and dried until constant weight and chopped to an average 0.5 mm particle size. The chopped material was kept in desiccator till use for no more than one week. The stock standard solutions (1,000 mg L^{-1}) of aluminium employed during the experiment were purchased from MERCK Company.

2.2. Factorial experimental design

Batch experiments were carried out under the following conditions: 50 ml of aluminium ions solution containing 7 mg L^{-1} Al^{3+} simulating its concentration in a real wastewater effluent, and an agitation speed of 100 rpm on a shaking water bath. The temperature, pH and initial phytomass weight employed are given in Table 1. Control samples were made in the absence of any metal. Solutions were collected after 120 min of equilibration as previously determined [12]. Solutions were filtered prior analysis for separation of biosorbent, and the residual aluminium concentrations were measured by inductively coupled plasma (ICP-OES, Perkin Elmer, model optima 2000 DV) at wavelength 396.153 nm with a detection limit of 0.0280 mg L^{-1}.

2.3. Biosorbent characterization

Infrared spectra of fresh-dried and metal-loaded *Typha* phytomass were obtained using a Fourier transform infrared spectrometer (Perkin-Elmer FT-IR 1650 spectrophotometer with working range 200–4,000 cm^{-1}). Elemental and fiber analyses of the biosorbent were performed using a Perkin Elmer Model 2400 elemental analyzer, (USA) and Fiber Analyzer Ankom 220 (Ankom Technology, Fairport, NY, USA), respectively. The biosorbent texture was examined using Scanning Electron Microscopy using an Electron Microscope model JEM-100s Joel (Japan). (Magnification: 50× →4000× and Acceleration: 40–60 kV).

Table 2
Experimental factorial design results for Al^{3+}uptake

Factor			Al^{3+}		
T	X	pH	Removal efficiency (%)		Average (%)
1	1	1	76.66	74.72	75.69
1	1	−1	3.67	4.78	4.23
1	−1	1	87.43	89.05	88.24
1	−1	−1	0.66	0.62	0.64
−1	1	1	80.56	82.75	81.65
−1	1	−1	1.17	1.52	1.34
−1	−1	1	88.97	89.46	89.22
−1	−1	−1	95.07	93.44	94.25

2. Results and discussion

2.1. Factorial design experiment results

Eight duplicate experiments were carried out. All possible combinations of variables, called factors in the jargon, were used, and a matrix was established according to their high and low levels, represented by +1 and −1, respectively [14] .The results for Al^{3+} removal percentages are given in Table 2.

The results were analyzed using the ''Minitab 15'' software (Minitab Ltd, USA) and the main effects and interactions between factors were determined. The effect of a factor is defined as the change in response produced by a change in the level of the factor. This is frequently called a main effect because it refers to the primary factors of interest in the experiment [15]. The main interaction effect, coefficients of the model, standard deviation of each coefficient and the probability as well as Student's *t*-test values for each effect for the full 2^3 factorial design for Al^{3+} are presented in Table 3.

The codified mathematical model employed for the 2^3 factorial design is

$$\begin{aligned} R = {} & A_0 + A_1T + A_2X + A_3pH + A_4TX \\ & + A_5T\text{pH} + A_6X\text{pH} + A_7TX\text{pH} \end{aligned} \tag{1}$$

where A_0 represents the global mean and A_i the other regression coefficients.

Table 3
Estimated effects and coefficients for Al^{3+} % removal (coded units)

Term	Effect	Coef	SE Coef	t	P
Constant		54.41	0.2456	221.56	0.000
Main factor					
T	−24.42	−12.21	0.2456	−49.72	0.000
X	−27.36	−13.68	0.2456	−55.71	0.000
pH	58.58	29.29	0.2456	119.28	0.000
Interaction of two factors					
TX	22.88	11.44	0.2456	46.58	0.000
TpH	20.95	10.47	0.2456	42.65	0.000
XpH	17.30	8.65	0.2456	35.23	0.000
Interaction of three factors					
TXpH	−25.37	−12.69	0.2456	−51.66	0.000

$S = 0.982258$ PRESS = 30.8746
R-Sq = 99.97% R-Sq(pred) = 99.88% R-Sq(adj) = 99.95%

Substituting the coefficients A_i in Eq. (1) by their corresponding values from Table 3 we get:

$$\mathrm{R}(\mathrm{Al}^{3+}) = 54.41 - 12.21T - 13.68X + 29.29\mathrm{pH} + 11.44TX + 10.47T\mathrm{pH} + 8.65X\mathrm{pH} - 12.69TX\mathrm{pH}$$

The main effects (T, X, pH) represent deviations of the average between high and low levels for each one of them. In the case of Al^{3+}, a change in pH value from low to high level resulted in 58.58% increase in the removal efficiency. If a variation from high to low level is made for temperature T and biosorbent weight X, decreases of, respectively, 24.42% and 27.36% in the removal efficiency are observed.

It can be concluded that when the effect of a factor is positive an increase in the value of the removal efficiency is observed when the factor changes from low to high level. In contrast, if the effect is negative, a reduction in removal efficiency occurs for the high level of the same factor [14]. Plots of the main effects are presented in Fig. 1.

It can be concluded that as a general trend an increase in pH increased the efficiency of metal ions removal by *Typha* biomass. It has been previously reported that biosorption capacities for heavy metals are strongly pH sensitive and that adsorption increases as solution pH increases [16–18]. At lower pH the overall surface charge on the adsorbent surface became positive and the presence of H^+ ions hinders the access of metal ions by repulsive forces to the surface functional groups, consequently decreasing the percentage of metal removal [19]. So at low pH level, uptake of metal ions was less, probably due to the cations competition effects with (hydronium) ions H_3O^+.Whereas on increasing pH the concentration of H_3O^+ decreases and that of OH^- increases on the surface of the adsorbent. The surface charge of the adsorbent thus changes to negatively charged sites which results in higher attraction of cations [20].

The data also showed that as a general trend metal ions removal decreased as temperature changed from low to high level, this decrease in adsorption with the rise in temperature may be due to the weakening of adsorptive forces between the active sites of the adsorbents and adsorbate species and also between the adjacent molecules of the adsorbed phase [21].The same trend was previously reported by Badr [22] which found that higher removal efficiency of Pb^{2+} by *E. Crassipes* biomass is detected at low temperature condition. Also Peternele et al. [23] reported a decrease in $Cd^{2+}$and Pb^{2+} biosorption onto *sugarcane bagasse* which they attributed to either the damage of active binding sites in the biomass or increasing tendency to desorb metal ions from the interface to the solution.

The decrease in ions removal, which was generally observed, when biosorbent dose increased from low to high level can be attribute to the formation of aggregates during biosorption which takes place at high biomass concentrations causing a decrease of the effective adsorption area. It is known that an increase in biosorbent concentration generally increases the adsorbed metal ion concentration because of an increasing adsorption surface area. But in several studies reported in the literature a decrease was found in the metal uptakes when the biomass concentrations were increased [18,24–26]. The researchers implied that a partial cell aggregation taking place at high biomass concentrations caused a decrease of active sites [10].

In the present study, as can be seen from Table 3 all the studied main factors and their interactions were significant at 5% of probability level ($P < 0.05$).

The results were also examined by means of Pareto charts (Fig. 2). The vertical line in Pareto charts indicates minimum statistically significant effect magnitude for a 95% confidence level.

In order to better evaluate each factor and its interaction in case of Al^{3+} (Fig. 3) presents the normal probability plot of standardized effects. The graph could be divided into two regions: the region with percent below 50%, where the factors and their interactions presented negative coefficients (T; X; TXpH) and the region with percent above 50%, where the factors and their interactions presented positive coefficients (pH; TpH; TX; XpH).

Analyzing the graphs of (Fig. 3) and the values of Table 3, it can be inferred that the pH was the most important variable of the overall biosorption procedure. The second important factor for overall optimization of

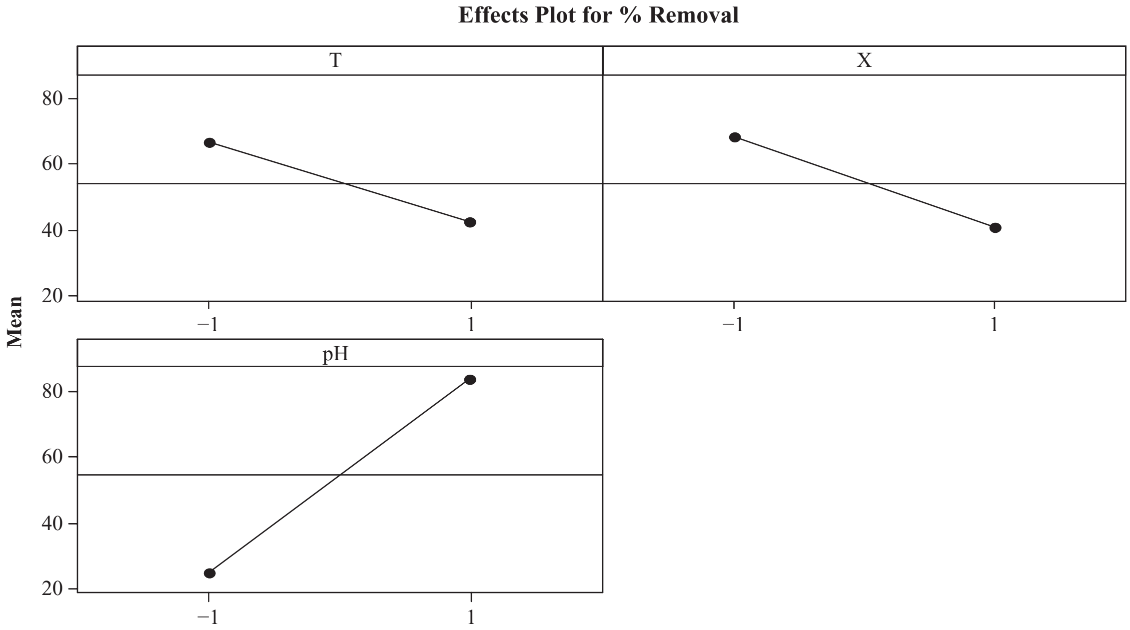

Fig. 1. Main effects plot for Al^{3+} % removal.

the batch system was the biosorbent weight (*X*). The third important factor affecting overall optimization of the batch system was the interaction between the three main factors *TX*pH. the negative value of *TX*pH coefficient means that low temperature with low pH and low biosorbent loading weight would lead to an increase in Al^{3+} removal%. The temperature was the fourth factor affecting removal, then comes the

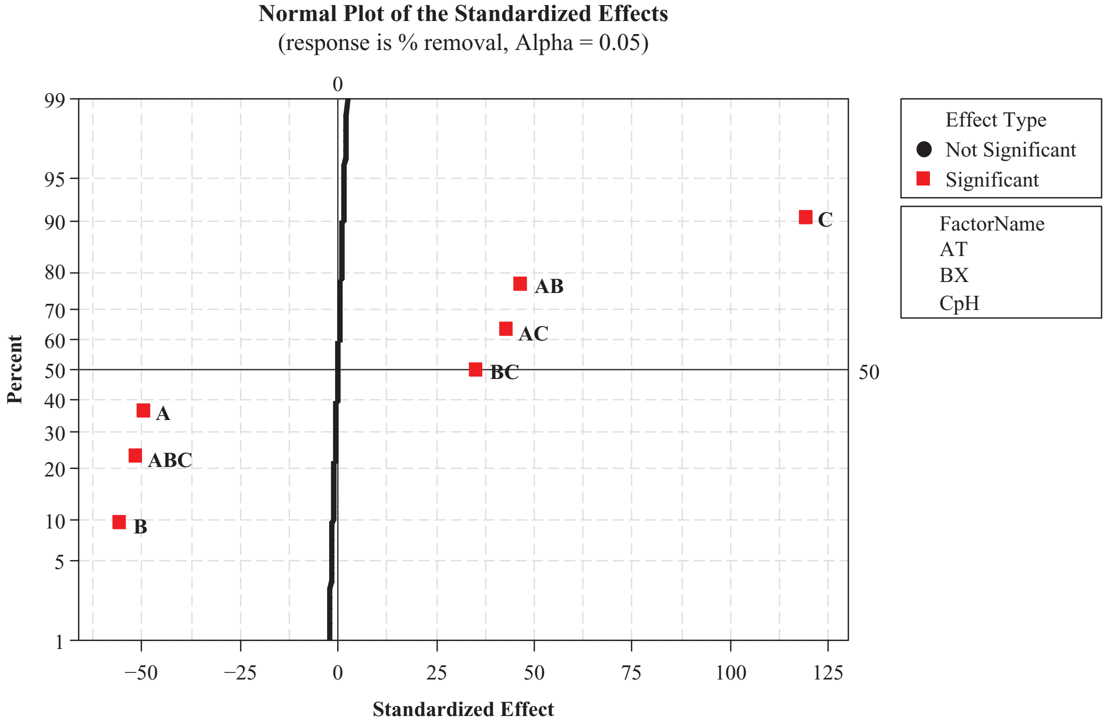

Fig. 2. Effects Pareto for Al $^{3+}$ % removal.

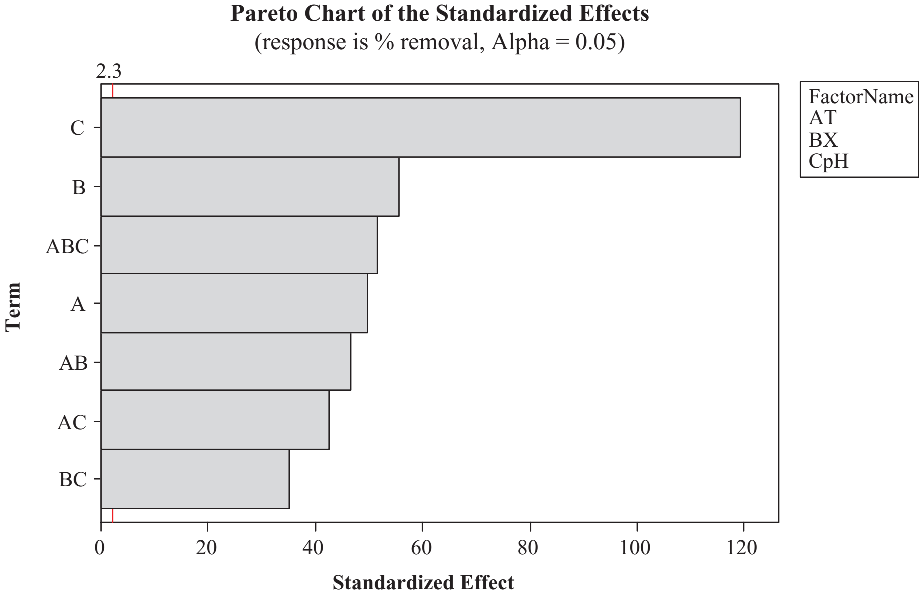

Fig. 3. Normal probability plot of the standardized effects for Al^{3+} removal%.

interaction *TX* followed by the interaction *T*pH and finally the interaction *X*pH with positive coefficient values meaning that the combination between high temperature and high biosorbent weight, the combination between high temperature and high pH and the combination between high biosorbent weight and high pH would lead to high removal efficiency.

Table 4 presents the analysis of variance for the factorial design 2^3 for Al^{3+}. As can be seen the main factors, two way interactions and three way interaction were significant at 5% of probability level ($P < 0.05$), as discussed above.

We should also examine the distribution of the residual values, defined as the differences between the predicted (model) and the observed (experimental) ones [15]. Fig. 4 presents the normal probability plot of residuals for removal efficiency of Al^{3+} also shows how closely the set of observed values follow a theoretical distribution. Noticing that, in all cases, experimental points were reasonably aligned suggesting a normal distribution.

Table 4
Analysis of Variance for Al^{3+} % removal (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	*F*	*P*
Main Effects	3	19107.3	19107.3	6369.11	6601.27	0.000
2-Way interactions	3	5046.4	5046.4	1682.12	1743.44	0.000
3-Way interactions	1	2574.8	2574.8	2574.80	2668.65	0.000
Residual error	8	7.7	7.7	0.96		
Pure Error	8	7.7	7.7	0.96		
Total	15	26736.2				

DF: degree of freedom. Seq SS: sequential sum of squares. Adj MS: adjusted sum of squares. F: factor F and P: probability.

2.2. biosorbent characterization

2.2.1. Elemental and fiber fraction analyses

Typha domingensis phytomass powder subjected to elemental analysis showed composition of carbon, hydrogen, nitrogen and sulphur as 43.35%, 10.06%, 2.49% and 1.21%; respectively as previously reported by [12]. *Typha domingensis* phytomass powder was also found to contain 31.17%, 34.09% and 4.16% hemicellulose, cellulose and lignin; respectively as previously reported by [13].

2.2.2. FTIR analysis

FTIR was used to analyze the functional groups in the fresh-dried *Typha domingensis* biomass. The results of FTIR spectra of the biosorbent *Typha* biomass, in native form and after aluminium ions adsorption, are depicted in Table 5. Interpretations of the spectra were based on the information acquired from the literature Interpretations of the spectra were based on the information acquired from the literature [4,27,28].

The FTIR spectra of fresh-dried (A) metal-loaded (B) *Typha* biomass are shown in Fig. 5. As can be seen the spectra display a number of absorption peaks,

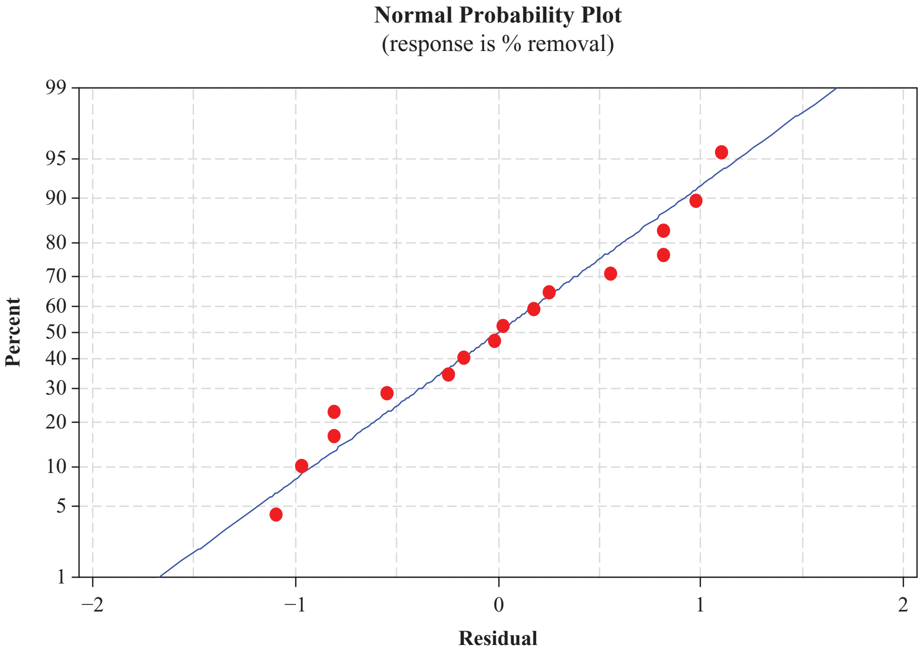

Fig. 4. Normal probability plot of residual for removal efficiency of Al^{3+}.

indicating the complex nature of the examined biomass. Table 5 shows the infrared absorption frequencies of each peak and the corresponding functional groups of *Typha* biomass as previously reported by Abdel-Ghani et al. [13]. This shift in the absorption peaks generally observed indicates that there is a metal-binding process taking place on the surface of *Typha* biomass [13].

Table 5
Surface functional groups observed on Typha biomass [12] by FTIR spectroscopy

Typha biomass before adsorption (cm^{-1})	*Typha* biomass after adsorption (cm^{-1})	Bond assignments
3400.85	3419.17	Bonded (O–H)/ N–H stretch
2921.63	2919.7	C–H stretching
1735.62	1736.58	C=O stretching of COOH
1641.13	1648.84	C=O (amide band)/ O–H (adsorbed water)
1424.17	1380.78	CH_2 & CH_3 deformation
1246.75	1247.72	–C–O stretching
1059.69	1057.76	C–O–C/stretching CN
603.1	612.288	OH (out of plane)

2.2.3. Scanning electron microscopy (SEM):

The surface morphology of Typha biomass is exemplified by the scanning electron micrograph in Fig. 6. As clearly seen here, the biomass seems to be fibrous and also it presents a lot of macro pores (pores with diameter higher than 50 nm). This surface property should be considered as a factor providing an increase in the total surface area [29–31].

So, based on the morphology of Typha biomass, as well as on the fact that it contains high amounts of cellulose and hemicellulose, it can be concluded that Typha biomass presents an adequate morphological profile to retain metal ions.

3. Conclusions

Typha domingensis phytomass was used as a biosorbent for aluminium ions removal from aqueous solution. The phytomass showed good removal efficiency towards aluminium removal. The total number of experiments in the present study was reduced by using the factorial experimental design. The three studied factors (T, X and pH) as well as their interactions significantly affected Al(III) removal. The study showed that pH was the most important factor affecting Al ions removal by *Typha domingensis* phytomass under the tested conditions. The second important factor for overall optimization of the batch system was the biosorbent weight (X). The third important factor affecting

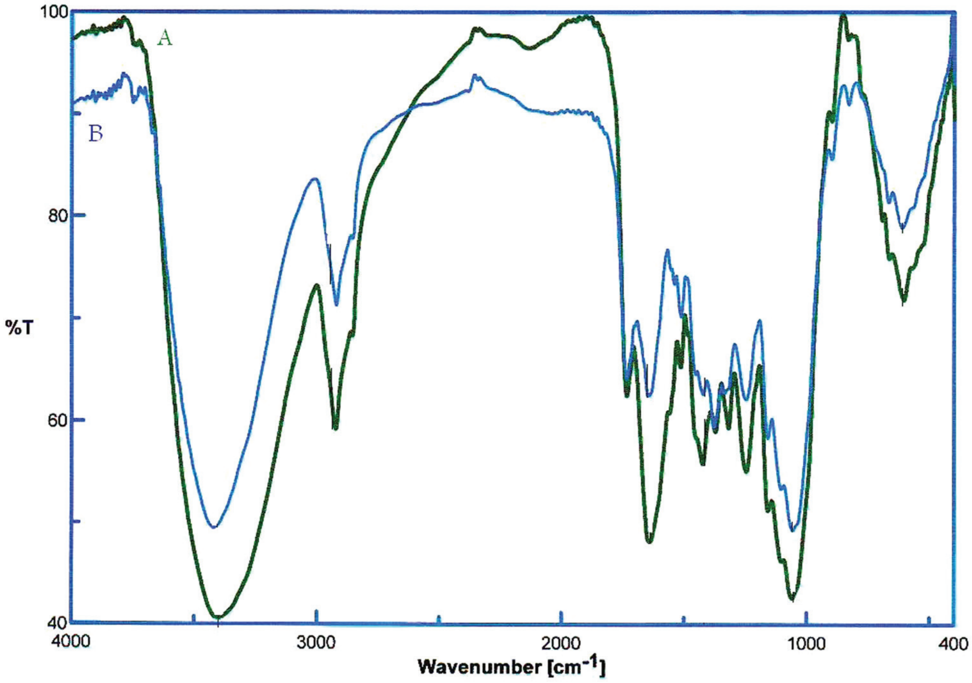

Fig. 5. FTIR spectra of fresh-dried (A) metal-loaded (B) *Typha domingensis* phytomass[12].

overall optimization of the batch system was the interaction between the three main factors *TX*pH showing that at low temperature (25°C), low pH value (2.5) and low biosorbent loading weight (0.5 g/50 ml) an increase in Al^{3+} removal% is achieved. The normal probability plot of residuals for removal efficiency of Al^{3+} showed how closely the set of observed values follow a theoretical distribution.

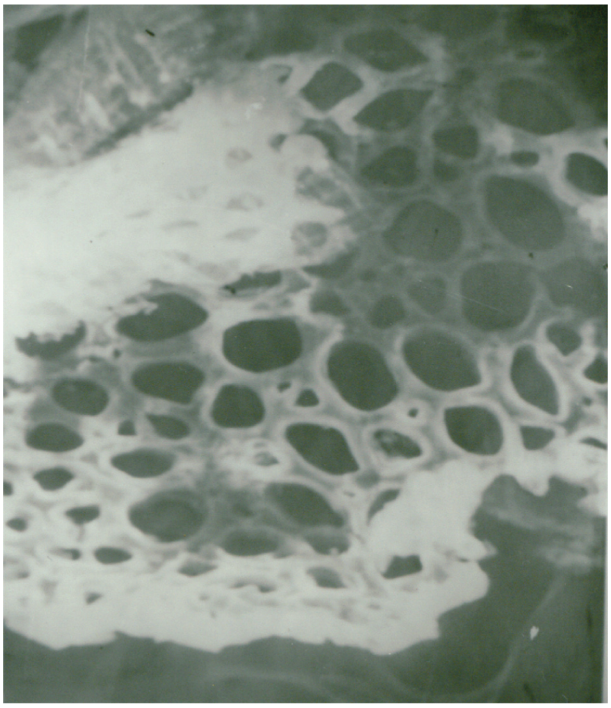

Fig. 6. Scanning electron micrograph of Typha biomass (×100).

The present study throws the light on a new environmental friendly adsorbent that can be used for industrial wastewater treatment. More studies could also be done for more optimization of the factors affecting biosorption process.

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