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Equilibrium Study of Cr (VI) Removal from Aqueous Solution by Stalks from Three Tobacco Species (*Nicotiana*) Grown in Bulgaria

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Agricultural and processing activities generate enormous amounts of tobacco waste, and the stalks left after harvesting of the leaves constitute a significant share. The stalks of common tobacco (*N. tabacum* L.) were considered a promising source for processing and recycling, but very little is known about the properties of the stalks from other *Nicotiana* species. The aim of the present study was to examine the performance of stalk powders from three *Nicotiana* species grown side-by-side in Bulgaria for the ability to remove Cr (VI) ions from aqueous solutions. The characterization of applied biosorbents was conducted by FTIR analysis. Batch experiments were carried out and the effects of different adsorption process parameters were determined. Maximum removal efficiencies of 99.13 ± 0.55%, 98.33 ± 0.58% and 95.00 ± 0.50% for *N. tabacum*, *N. rustica* L. and *N. alata* Link&Otto, respectively, were obtained at pH 3.0, adsorbent dosage 5 g/L, initial Cr (VI) concentration 10 mg/L, temperature 25.0 ± 0.5oC, agitation speed 200 rpm and contact time 60 min. The Langmuir and Freundlich models fitted well the equilibrium isotherms experimental data. Based on the values determined for the maximum adsorption capacity, the powder from *N. alata* stalks was found to have higher affinity (9.87 mg/g) for Cr (VI) ions than those obtained from *N. tabacum* (8.38 mg/g) and *N. rustica* (6.96 mg/g) stalks.

Keywords: chromium, water, tobacco, stalks, biosorption.

Introduction

Heavy metal pollution has become a serious problem nowadays, reflecting the fact that these toxic elements easily accumulate in the food chain and subsequently affect all living organisms in a given biological system (Zhang et al., 2019). The raw and wastewaters infiltrated with heavy metals have to be treated, because they threat both the ecosystems and public health. It is well established that heavy metals are non-degradable and causing various diseases and disorders (Dahlan et al., 2013; Contreras et al., 2015).

Chromium (VI) is commonly used in tanning, electroplating, pigmentation, wood preservatives, cement, steel, ceramic and glass industries and has been considered among the top sixteen toxic pollutants with harmful effects on human health (Gardea-Torresday et al., 2000; Pehlivan et al., 2012; Owalude & Tella, 2016). The conventional wastewater treatment methods used for removal of Cr (VI) have been reported to be expensive and not efficient for initial Cr (VI) concentrations ranged from 10 to 100 mg/L (Sen & Dastidar, 2011).

In recent years, much attention has been paid to the adsorption of heavy metals and it has become one of the most frequently used methods for wastewater treatment, due to its simplicity in handling and relatively low exploitation price (Zhang et al., 2019). In the last decades, there has been a tendency to use natural biosorbents, especially waste materials, because of their low price, large availability, high efficiency, biodegradability and safety. Most of the adsorption studies have considered on using plant waste, because such lignocellulose materials carry a large number of functional groups, which have affinity to bind metal ions (Gardea-Torresday et al., 2004; Wang & Chen, 2009). Agricultural waste, like stalks, stems, shells, husks, hulls, peels, etc., has been reported to possess the ability to absorb heavy metals from aqueous solutions (Demirbas, 2008; Hlihor & Garvilescu, 2009; Nandini et al., 2015).

Tobacco is an important crop with special economic value. Although the genus (*Nicotiana*) integrates over 70 species, only two of them – *N. tabacum* L. (common tobacco) and *N. rustica* L. (Aztec tobacco, makhorka) – are commercially cultivated for tobacco products. Bulgaria is historically recognized as a producer and exporter of tobacco, especially for the high-quality aromatic Oriental ecotypes, and according to the national statistics (MAFF, 2018), the annual tobacco production estimates to about 13,000 t (dry leaf) from over 7,700 ha of harvested land. The large-scale agricultural and processing activities generate an impressive amount of tobacco waste worldwide, which constitutes a serious environmental problem (Li et al., 2008; Shakhes et al., 2011). The usable part of the plants are the leaves (approx. 30% of the biomass), while the rest of it (i.e., stalks, flowers, seeds) remain unutilized and turn into waste. Tobacco stalks in particular constitute about 50–60% of the available biomass, but are disposed of as waste, buried into soil or burned in the field after the leaf is harvested. There are several research papers investigating the properties of tobacco stalks, evaluating them as a promising material for the pulp and paper industry (Agrupis et al., 2000; Shakhes et al., 2011), for obtaining plywood (Jimenez & Acda, 2018) and biomass briquettes (Bozukov et al., 2013; Li et al., 2014; Radojičić et al., 2014; Xinfeng et al., 2015), for biofuel production (Bragatto et al., 2016) or for the isolation of chemicals (Akpinar et al., 2010). The rest of the *Nicotiana* species are considerably less studied, although they are all capable of intensive biosynthesis of multiple secondary metabolites with biological and pharmacological activities (Jassbi et al., 2017), and to the best of our knowledge, there are no reports about the specific composition, properties or use of their discarded stalks.

A few reports have been presented in the literature for the ability of tobacco waste to remove heavy metals from aqueous solutions (Sheth & Soni, 2004; Li et al., 2008; Qi & Aldrich, 2008; Chen et al., 2009). However, there have been a relatively small number of articles about the application of tobacco stalks for biosorption of Cr (VI) from aqueous solutions. Therefore, the aim of the present study was to investigate the ability of the stalk powder from different *Nicotiana* species grown in Bulgaria to remove Cr (VI) ions from aqueous solutions.

Methods

Materials

In the present study, residual tobacco stalks from three *Nicotiana* species were used. Common tobacco (*N. tabacum* L.) was a local Oriental ecotype, and the other two were *N. rustica* L. (Aztec tobacco, makhorka) and *N. alata* Link&Otto (jasmine or flowering tobacco). The plants were grown side-by-side under identical environmental conditions in the field of the Tobacco and Tobacco Products Institute, Markovo, Bulgaria. The collected stalks were transformed to powders by cutting, drying (40°C), milling (Bosh MKM 6003, Germany) and sieving through a 1.0 mm sieve. Finally, biosorbents were stored in plastic bags for further use.

Fourier transform infra-red (FTIR) spectroscopy was used for the identification of functional groups available in the biosorbents. The FTIR spectra of the samples were collected on a Bruker Tensor 27 (Bruker, Germany) spectrometer, equipped with a KBr beam splitter and OPUS 6.5 software. The spectra were recorded over a wavenumber range of 4000–400 cm^{-1} at 132 scans with a spectral resolution of 4 cm^{-1}.

All reagents used in the experiments were of analytical grade. Stock solution (500 mg/L) of Cr (VI) was prepared by dissolving of $K_2Cr_2O_7$ in distilled water. The solution was further diluted with distilled water to obtain the working solutions for the batch experiments study. The pH value of the samples was adjusted by adding 0.1 M NaOH or HCl, respectively.

Biosorption batch experiments

Biosorption experiments were carried out in 250 mL Erlenmeyer glass flasks with 100 mL Cr (VI) solution. Batch experiments were carried out to determine the effect of pH (1.0, 2.0, 3.0 and 4.0), initial Cr (VI) concentration (10, 20, 30, 40, 50 and 100 mg/L) and biosorbent dosage (1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 g/L). All experiments were carried out at a temperature of 25.0 ± 0.5°C, contact time of 60 min and agitation speed of 200 rpm, based on preliminary study.

Analytical methods

In order to determine Cr (VI) concentration in the solutions before and after biosorption, the samples were vacuum filtered (MN640 de filter paper) and the filtrate was analyzed at 540 nm according to the standard diphenilcarbazide method (APHA, 1992).

The equilibrium metal uptake q_e (mg/g) was determined by employing the following mass balance (1):

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{1}$$

Where: q_e – the equilibrium metal uptake (mg/g);

C_0 - C_e – the initial and the final metal concentrations (mg/L);

m – the mass of biosorbent material (g);

V – the initial volume of Cr (VI) solution (L).

The performance of biosorption was evaluated in terms of its removal efficiency as RE (%), estimated by the following equation (2):

$$RE = \frac{(C_0 - C_t) \cdot 100}{C_0} \tag{2}$$

Where: RE– the removal efficiency (%);

C_t – Cr (VI) concentration (mg/L) at a given time t.

Equilibrium isotherm study

Isotherm study is important to establish the most appropriate correlations for the equilibrium data of the system for optimizing the adsorption process (Febrianto et al., 2009). Equilibrium sorption experiments were performed as follows: 0.5 g of biosorbent were exposed to a 100 mL Cr (VI) solution with initial concentrations from 10.0 to 100.0 mg/L at constant pH 3.0, agitation speed 200 rpm and ambient temperature 25.0 ± 0.5°C for 120 min in order to reach equilibrium. Adsorption isotherm was plotted as the sorbate uptake (q_e) versus the equilibrium concentration of the residual sorbate remaining in the solution (C_e). The Freundlich (1906) and the Langmuir (1918) isotherm models and their linearized forms were used to correlate the equilibrium data for Cr (VI) removal.

Statistical analysis

All experiments were run in triplicate. The data were analysed and presented as mean values. Statistical techniques, incl. ANOVA and Duncan's Multiple Range Test were applied to determine the significant differences at a 95% confidence ($P < 0.05$) level.

Results and Discussion

FTIR characterization of biosorbents

The three biosorbents used in the present study were subjected to the FTIR spectral analysis in order to reveal the presence of functional groups available for Cr (VI) binding in aqueous solutions. The acquired FTIR spectra of the biosorbents are presented in Fig. 1 and the assignments of the characteristic bands in Table 1.

Fig. 1. *FTIR spectra of the stalk powders from N. alata (a), N. tabacum (b) and N. rustica (c).*

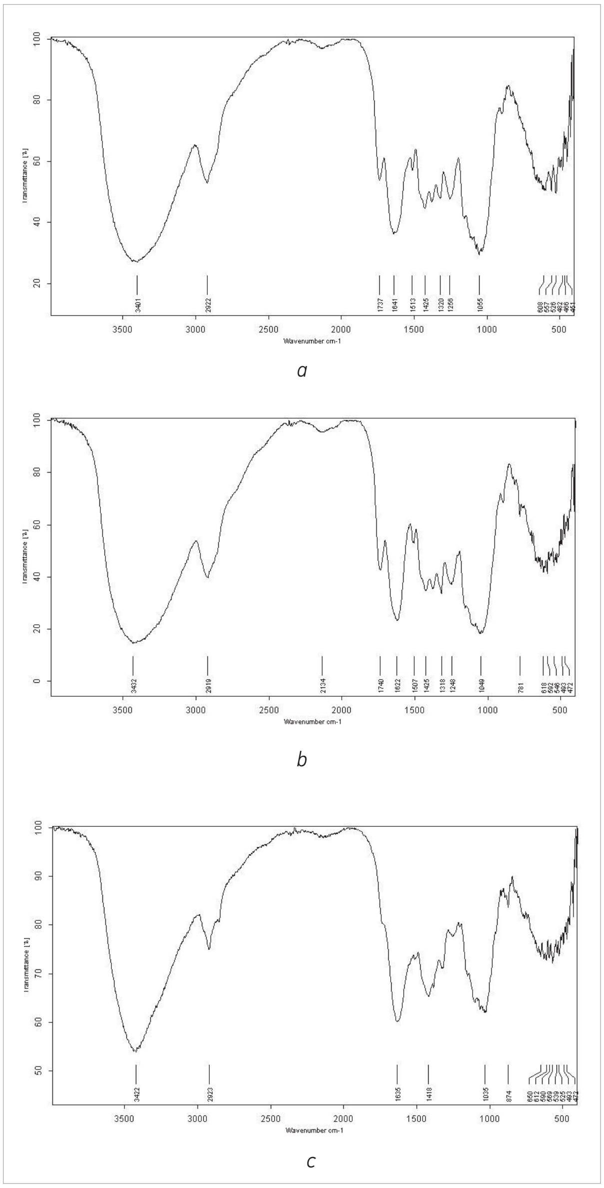


Table 1. *Assignments of the characteristic bands in the FTIR spectra of stalk powders from N. alata, N. tabacum and N. rustica*

Characteristic bands (cm-1)			Assignments
NA	NT	NR	
3,401	3,432	3,422	γ–OH bond, probably intramolecular H-bond (3,550–3,400 cm-1).
2,922	2,919	2,923	Characteristic band of –CH2–γas group (2,940–2,915 cm-1).
nd	1,740	nd	Cyclic ketone, characteristic band of cyclopenthanone (1,750 – 1,740 cm-1).
1,737	nd	nd	Aliphatic system –CH2–CHO aldehyde (1,740–1,720 cm -1) highly eroded strip. Participation in the formation of the H-bond.
nd	1,622	1,635	γC=O, characteristic band of unsaturated carbonyl compounds (1,650–1,620 cm-1).
1,641	nd	nd	Non-conjugated C = C, low intensity. HRC = CH2 end vinyl group.
1,513	1,507	nd	Carcass vibrations of aromatic ring, γC = C (1510–1480 cm-1)
1,425	1,425	1,418	Characteristic band of vibration of δCH2.group in a ketone –CH2–CO– (1,435–1,405 cm-1).
nd	1,318	nd	Primary alcohol pronounced band (1,350–1,206 cm-1)
1,320	nd	nd	Characteristic band of –OH group adjacent to γ–CO (1,320–1,080 cm-1).
1,256	1,248	nd	Characteristic band of ether γasC–O–C (1,260–1,240 cm-1)
1,055	1,049	1,035	Characteristic band of aromatic and vinyl =C–O–C; γsC–O–C in this band are with lower intensity (1,070–1,020 cm-1)
nd	nd	874	Trisubstituted aromatic ring γAr–H in positions 1,2,4 (900–865 cm-1)
nd	781	nd	Trisubstituted aromatic ring γAr–H in positions 1,2,3 (800–755 cm-1)

N, N. alata; NT, N. tabacum; NR, N. rustica; nd, not detected.

The IR spectral analysis showed that all biosorbents had a number of functional groups, which potentially would be involved in the removal of Cr (VI) ions from aqueous solutions. Although each of the three samples represented lignocellulose stalk material, there was some differentiation between the biosorbents on a species basis. For example, the spectra of *N. tabacum* and *N. rustica* had distinctive bands at 874 cm^{-1} and 781 cm^{-1}, respectively, characteristic of trisubstituted aromatic rings at different positions (800–755 cm^{-1}, 900–865 cm^{-1}), which were absent in the spectrum of *N. alata*. The latter, together with *N. tabacum*, had absorption bands in the range 800–755 cm^{-1}, corresponding to a γ^{as} ether group not found in the spectrum of *N. rustica*. These examples and the rest of the data presented in Table 1 correlated to the different Cr (VI) removal efficiency of the biosorbents under the conditions of the batch experiments and the isotherm studies.

Effect of pH

The pH of the aqueous solutions is an important parameter since it affects the surface charge of the sorbent and the degree of speciation and ionization of the sorbate during adsorption (Dahlan et al., 2013). Determination of the optimal pH value, i.e., the value at which the maximum metal removal efficiency is achieved is a point of great practical importance (Tavlieva et al., 2015). The effect of pH on Cr (VI) removal efficiency from the aqueous solution by the studied biosorbents is illustrated in Fig. 2.

Maximum removal efficiency was found at pH = 3.0 for stalk powders from all tested tobacco species. Ali et al. (2016) also reported that pH = 3.0 was the optimum for maximum uptake of Cr (VI) by using grafted banana peels as adsorbent. Most studies also reported maximum removal efficiency of Cr (VI) at low pH, indicating that chromium existed as negatively charged $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-} forms, while the positively charged surface of the adsorbent enhances the sorbent-sorbate interaction at low pH, thus resulting in high Cr (VI) removal (Blázquez et al., 2009; Prasad & Abdullah, 2010; Gupta et al., 2011; Pehlivan et al., 2012; Gill et al., 2014; Ali et al., 2016).

Effect of adsorbent dosage

The removal of Cr (VI) from aqueous solutions by using stalks powders from *N. alata*, *N. tabacum* and *N. rustica* tobaccos as a function of biosorbent dosages is presented in Fig. 3.

The Cr (VI) removal efficiency was observed to increase with the increase in biosorbent dosage up to 5.0 g/L, but it then decreased for all investigated biosorbents. The increase in metal removal efficiency can be explained by availability of more surface area for contact between the adsorbent and the adsorbate, as reported similarly by other studies (Sheth & Soni, 2004; Ali et al., 2016).

Fig. 2. *Effect of pH on the removal efficiency of Cr (VI) from the aqueous solution by stalk powders from N. alata, N. tabacum and N. rustica (initial metal concentration 10 mg/L, biosorbent dosage 1 g/L, 25°C, 60 min, agitation speed 200 rpm).*

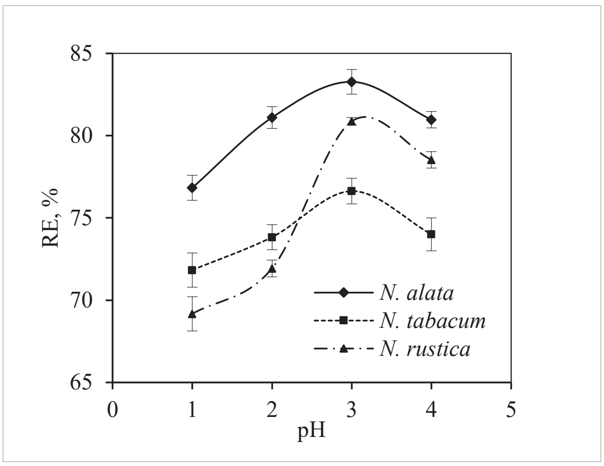
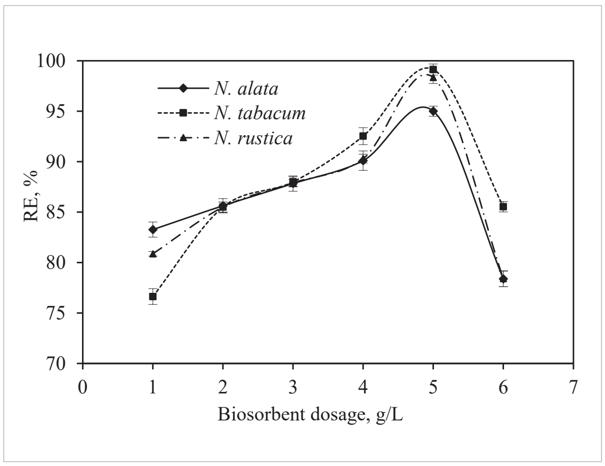


Fig. 3. *Effect of biosorbent dosage on the removal efficiency of Cr (VI) from the aqueous solution by stalk powders from N. alata, N. tabacum and N. rustica (initial metal concentration 10 mg/L, biosorbent dosage 1 g/L, 25°C, 60 min, agitation speed 200 rpm).*



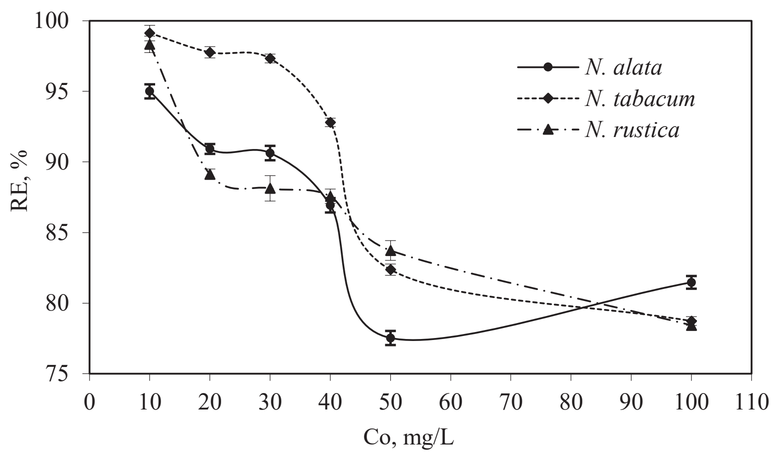
Effect of initial metal concentration

The results on the influence of the initial Cr (VI) concentration in the solution on metal removal efficiency are presented in Fig. 4. The highest level of removal efficiency (99.13 ± 0.55%, 98.33 ± 0.58% and 95.00 ± 0.50%) was established at an initial metal concentration of 10 mg/L for the stalks of *N. tabacum*, *N. rustica* and *N. alata*, respectively. The removal efficiency of Cr (VI) ions from aqueous solutions by the biosorbents studied was found to decrease with the increase in the initial metal concentration, probably due to the restriction or saturation of the biosorbent active groups. Similar results have been reported by other researches for the biosorption of Cr (VI) ions from aqueous solutions (Venkateswarlu et al., 2007; Acharya et al., 2009; Prasad & Abdullah, 2010).

Equilibrium isotherms data

Equilibrium adsorption isotherms study is of fundamental importance in the design of adsorption systems. An adequate mathematical modelling of the experimentally obtained isotherms is essential for the efficient design of the systems (Febrianto et al., 2009, Bhatti et al., 2010).

Fig. 4. *Effect of initial metal concentration (C0, mg/L) on the removal efficiency of Cr (VI) from the aqueous solution by stalk powders from N. alata, N. tabacum and N. rustica (initial metal concentration 10 mg/L, biosorbent dosage 1 g/L, 25°C, 60 min, agitation speed 200 rpm).*



In the present work, the isotherm models of Langmuir and Freundlich, as two of the most frequently used models (Acharya et al., 2009), were tested, and the isotherm parameters determined by applying linear regression are summarized in Table 2. The values of the obtained coefficients of determination (R^2) indicate that the Langmuir and Freundlich models fitted very well the experimental data. Similar results were reported by other studies (Sheth & Soni, 2004; Venkateswarlu et al., 2007; Acharya et al., 2009; Gupta et al.,

Table 2. *Isotherm parameters of Langmuir and Freundlich models for biosorption of Cr (VI) ions onto tobacco stalks powders*

Biosorbent	Langmuir isotherm model			Freundlich isotherm model		
	q_{max} (mg/g)	K_L (L/mg)	R^2	1/n	K_F (mg/g)	R^2
N. alata	9.87	0.461	0.958	0.5431	2.76	0.951
N. tabacum	8.38	3.470	0.943	0.3384	5.06	0.946
N. rustica	6.96	2.314	0.839	0.4191	3.49	0.928

2011). The value of R^2 for the Langmuir model was slightly higher for *N. alata* stalks, while that for the Freundlich model was higher for the other two biosorbents.

The values of the separation factor taken from the Langmuir isotherm analysis were found to be between 0 and 1 for all biosorbents applied, which indicated that the biosorption of Cr (VI) ions from aqueous solutions is favourable under the conditions of this study (Foo & Hameed, 2010). Moreover, the 1/n values less than 1 implied a stronger interaction between the biosorbents and Cr (VI) ions and favourable adsorption, as reported similarly by Acharya et al. (2009).

Based on the values of the maximum adsorption capacity (q_{max}, mg/g), a comparison between different biosorbents used for Cr (VI) removal from aqueous solutions was carried out and the results are presented in Table 3. The obtained data indicated that the investigated tobacco stalk powders possess sufficient adsorption capacities compared with other biosorbents.

Table 3. *Reported adsorption capacities for biosorption of Cr (VI) ions for different biosorbents*

Biosorbent	Adsorption capacity (qmax) (mg/g)	Reference
Tobacco stalks powder *N. alata* *N. tabacum* *N. rustica*	 9.87 8.38 6.96	Present study
Chemically modified banana peels	6.17	Ali et al., 2016
Potato/carrot peels (1:1 ratio)	1.089	Gill et al., 2014
Activated coconut shell Activated coconut coir	5.319 7.849	Gupta et al., 2011
Gulmohar's fruit shell	12.28	Prasad and Abdullah, 2010
Walnut shell Hazelnut shell Almond shell	8.01 8.28 3.40	Pehlivan and Altun, 2008
Pre-boiled sunflower stem Formaldehyde-treated sunflower stem	5.37 4.80	Jain et al., 2009
Walnut hull	98.13	Wang et al., 2009
Modified groundnut hull	131	Owalude and Tella, 2016
Osage orange peel Osage orange pulp	93.67 84.26	Pehlivan et al., 2012

Conclusions

The results from the present study indicated that stalk powders from *N. alata, N. tabacum* and *N. rustica* could be applied as low-cost biosorbents for the removal of Cr (VI) ions from aqueous solutions. Biosorption batch experiments showed that maximum removal efficiencies of 99.13 ± 0.55%, 98.33 ± 0.58% and 95.00 ± 0.50% for *N. tabacum*, *N. rustica* and *N. alata,* respectively, were obtained at pH = 3.0, adsorbent dosage 5 g/L, initial Cr (VI) concentration 10 mg/L, temperature 25.0 ± 0.5°C, agitation speed 200 rpm and contact time of 60 min. The adsorption isotherms followed the Langmuir model (R^2 = 0.958) for *N. alata* stalks and the Freundlich model (R^2 = 0.946 and R^2 = 0.928) for *N. tabacum* and *N. rustica* stalks. Finally, the tobacco stalk powder from *N. alata* was found to have a higher adsorption capacity for Cr (VI) ions removal from the aqueous solution than those from *N. tabacum* and *N. rustica*.

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