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SORPTION DYNAMICS OF DIRECT ORANGE 26 DYE ONTO A CORNCOB PLANT SORBENT

DYNAMIKA SORPCJI BARWNIKA DIRECT ORANGE 26 NA SORBENCIE ROŚLINNYM - KOLBACH KUKURYDZY

Abstract: The azo dye and plant-derived sorbent system was investigated in this paper. Direct Orange 26 azo dye was acquired from Boruta-Zachem Kolor Sp. z o.o. Chemically modified granulated corncobs obtained from Chipsi Mais Germany were used as the biosorbent. The changes in the dye and sorbent concentrations with time were measured and used for further calculations. The experiments were carried out in a laboratory fixed bed column. Breakthrough curves were plotted for different initial concentrations, volumetric flow rates and bed heights. Sorption dynamics was described by a model presented in the literature. It was demonstrated that Infrared analysis of the system allows to determine the nature of the dye-sorbent bond. It was found that corncobs can be used as a promising sorbent material.

Keywords: azo dye, corncobs, sorption dynamics, fixed bed column

Introduction

Water is essential for life and economy. It is used for consumption, personal hygiene and it is required for the development of industry, farming and other sectors. At present, it is extremely important to maintain the standards of water quality set by applicable regulations and eliminate harmful substances from wastewater before it is discharged to the ecosystem. Technology options in water treatment include oxidising, ion exchange, adsorption, extraction, coagulation, sedimentation, ultrafiltration, neutralisation etc. [1].

Despite progress in technology and the use of modern equipment facilities, the textile industry is still very water intensive. As a result, vast amounts of wastewater are produced that cause environmental damage. In the textile industry, wastewater quality composition largely depends on which of the tens of thousands of dyes available on the market are used [2]. Effluents are salt laden, alkaline and most importantly, have intense colours. They are produced by the dyeing industry are decoloured primarily using synthetic ion-exchange beds which are highly effective. However, they are costly and difficult to dispose of. As a result, researchers are now exploring the potential to use natural waste products as sorbents (*eg* rye straw, vegetable peels, grain seed hulls, algae or biomass in a broad sense

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of the term) [3-10]. They are relatively cheap and biodegradable which makes them an attractive alternative to synthetic substances.

In this paper, adsorption of Direct Orange 26 azo dye onto a plant sorbent *ie* granulated corncobs was analysed. After initial studies with raw and boiled cobs, further experiments involved cobs which had been chemically pretreated with a view to increasing their sorption capacity. Experiments were carried out to determine sorption kinetics and equilibrium based on the changes of dye concentration in the solution and in the sorbent. The primary goal of the study were sorption dynamics experiments conducted in the column packed with a modified sorbent.

The parameters analysed were: sorbent-dye solution contact time, bed breakthrough and saturation time. Based on the data obtained, the efficiency of Direct Orange 26 azo dye removal was determined for different process parameters. The results were described mathematically using a model proposed in the literature that describes the change in the amount of dye adsorbed on the bed in the column q [mg/g] based on the obtained breakthrough curves, *ie* $C = f(t)$.

Materials

The dye used for the study was supplied by Boruta-Zachem Kolor Sp. z o.o. in Zgierz and belongs to a group of azo dyes. Chemical structure of the dye is presented in Figure 1.

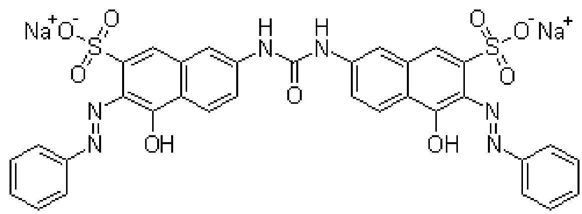

Fig. 1. Molecular structure of Direct Orange 26, molecular formula: $C_{33}H_{22}N_6Na_2O_9S_2$, MW = 756.67

Fig. 2. Granulated corncobs

Granulated corncobs were used as a sorbent. Cobs are the thick, hard central core of maize. They are a lignocellulosic material composed of 44-45% cellulose, 31-40% hemicellulose, and 8-15% lignin [11, 12]. Corncobs used in the study were acquired from

CHIPSI MAIS Germany. They were hard granules of the mean size of approximately 0.005 m, humidity of approximately 10%, and density of 438.8 kg/m^3. Figures 2 and 3 show the granulated sorbent and the photo of its surface. Apart from being used for dye sorption, corncobs are also reported to be widely used for removal of heavy metals from aqueous solutions [13-16]. Corncobs are also equally commonly used to obtain activated carbon [17-21]. Activated carbon obtained from corncobs is used to adsorb several water contaminants such as methylene glycol [22], chlorophenol [23], dyes [24] or heavy metal ions [16, 25-27].

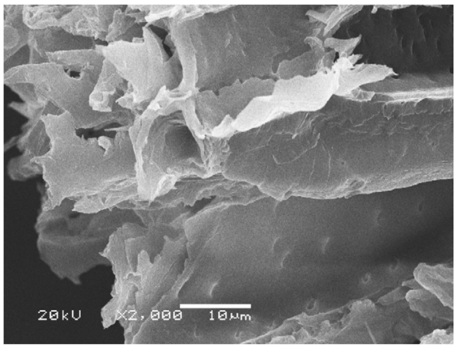

Fig. 3. SEM photo of corncob surface (2000x) [26]

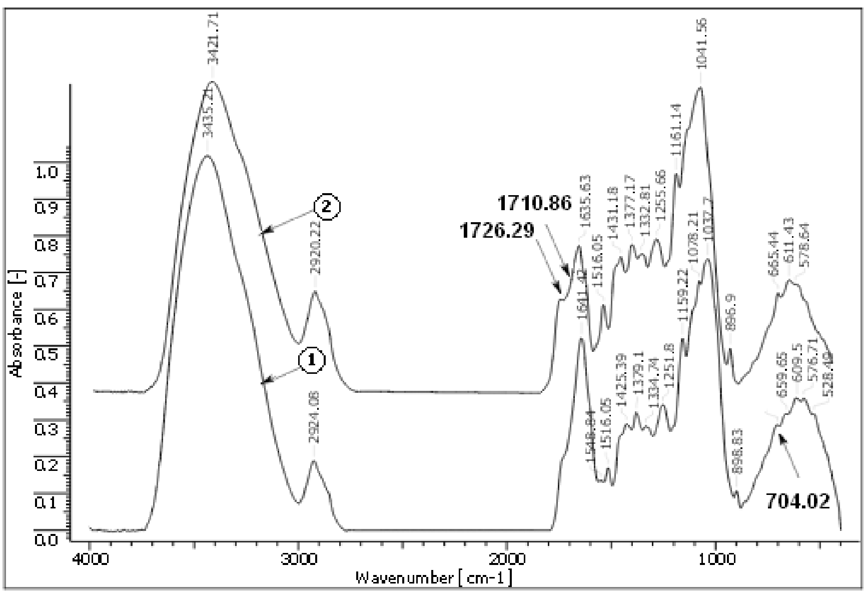

Fig. 4. FTIR spectra for: 1) corncob, 2) corncob with Reactive Orange 16 [28]

Infrared analysis of the sorbent is used both prior and after dye adsorption process to explore the mechanism of dye compound binding onto the sorbent. This allows to observe the modifications and bonds between the lignocellulosic complex of the biosorbent and the adsorbed contaminant.

Literature [28] describes the mechanism of Reactive Orange 16 azo dye binding onto corncobs (at pH = 1). Figure 3 compares the spectra for corncobs prior to and after dye adsorption. Specific bands can be observed at 1710.86 and 1726.29 cm^{-1}, which indicates that ionic bonds are formed between lignin and the dye. At acidic pH, due to the presence of hydroxyl groups of the side chain, lignin can be converted into conjugated structures with deficit electron centre (δ+), as shown by the band at 704.02 cm^{-1} (none on line 2). The authors conclude that FTIR spectra suggest a combined sorption mechanism being the result of ion exchange interactions and physical sorption.

The authors [29] report on the absorption spectra of dyes for several cheap plant sorbents such as birch chips, rice straw, hemp fibre and cellulose. Figure 5 shows a comparison of absorption spectra for cellulose as the sorbent and different azo dyes. A similar relationship was observed for cellulose and rye straw with the exception of Direct Orange 26, in which case the spectrum is totally different and new absorption bands appear (that were observed neither for the dye nor for the material itself). It means that the dye reacts with the molecular entities in the layer. Detailed analysis indicates the formation of assemblies such as sulphonic acids, thioketones (sulphoketonic forms - partially oxidised to acids) and acid esters (reciprocal reaction products).

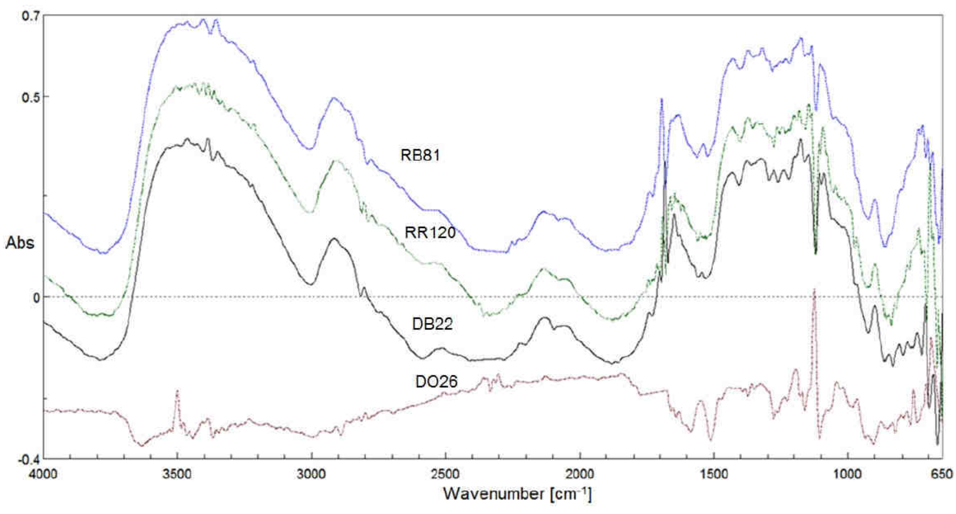

Fig. 5. Comparison of IR spectra obtained for cellulose after adsorption of four dyes: Reactive Blue 81, Reactive Red 120, Direct Black 22, Direct Orange 26 [29]

Dye binding to the sorbent may be the result of weak van der Waals forces and strong ionic exchange interactions between ionised sulfonic groups of the dye and sorbent surface as per the following formula [28]:

$$\text{Corncob} - \text{OH} + \text{H}^+ + \text{O}_3\text{S} - \text{Dye} = \text{Corncob} - \text{OH}_2^+ + \text{H}^+ + \text{O}_3\text{S} - \text{Dye}$$

Test method

Granulated corn cobs were washed and boiled for 3 h in a pressure cooker (130ºC). To increase their sorption capacity, the corncobs were etched with 10% H_2SO_4 for 5h at 60ºC. Following chemical pretreatment, the granulated corncobs were dried at 70ºC for 2 h. The procedure of chemical pretreatment was developed based on the previous experience with corncobs that had only been washed. Sorption equilibrium and kinetics studies were carried out at T = 25ºC, pH = 5-6. Five grams of dry weight sorbent were placed in glass flasks and 200 cm^3 of the solution of dye concentration of 100-800 mg/dm^3 was added. Flasks with the mixture were shaken mechanically in a water bath until adsorption equilibrium was reached. During the process, dye concentration in the water phase was measured using UV-vis Jasco V630 spectrophotometer at wavelength of 494 nm. Based on experimental data, with known initial concentration C_0 and equilibrium concentration C_e, sorption capacity q_e was determined for the solution using the following formula:

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

where: C_0 and C_e - initial and equilibrium concentration of dye in the solution [mg/dm^3], q_e - equilibrium concentration of dye in the adsorbent, sorption [mg/g], V - solution volume [dm^3], m - adsorbent mass [g].

Sorption kinetics results are presented in Figure 6.

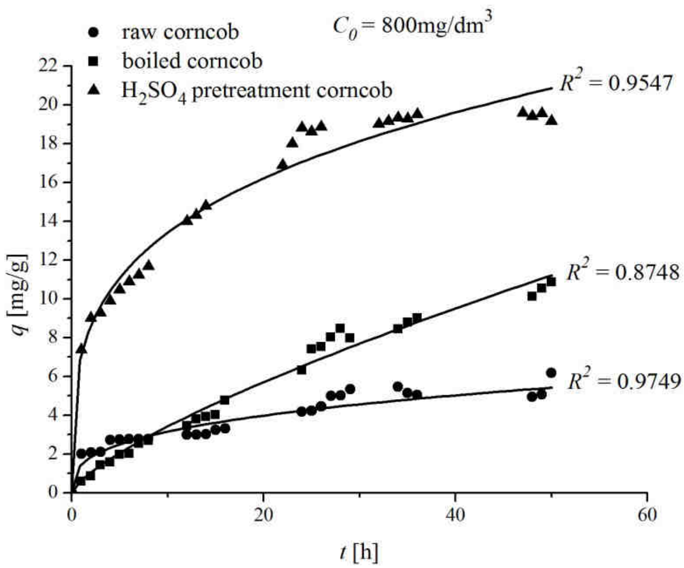

Fig. 6. Dye sorption kinetics for different methods of sorbent pre-treatment

Adsorption dynamics studies were conducted in a laboratory column of 3.45 cm in diameter and 70 cm in length (Fig. 7) packed with granulated corncobs. Bed porosity was ε = 0.33. Dye solution (flowing upwards) was fed with a dosing pump. Having passed through the bed, it was collected at predetermined intervals and analysed quantitatively using UV-Vis Jasco V630 spectrophotometer, pH and temperature of the dye solution was measured at the column inlet and outlet. Temperature stabilized at approximately 25ºC, and pH was approximately 5-6. Experiments were conducted for two initial concentrations of dye solution C_0 = 50 and 75 mg/dm^3, four volumetric flow rates Q = 50, 100, 200 and 400 cm^3/h and two bed heights H = 59 and 29 cm, which corresponded to mass m = 165 and 85 g.

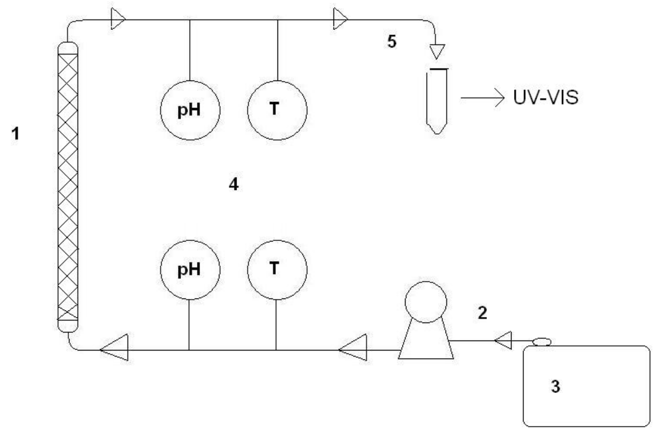

Fig. 7. Experimental setup: 1 - column, 2 - dosing pump, 3 - dye tank, 4 - temperature and pH measurements, 5 - sampling

Mathematical description of sorption equilibrium

Sorption equilibrium mathematical modelling is useful for analysing and designing adsorption systems. Dynamics description defines the change of the concentration of adsorbate in the solution and adsorbent over time and along the bed height. For the packed column it was assumed that the process was isothermal, the bed was uniform and constantly porous, adsorbate flow rate and feed solution concentration were constant.

To determine q [mg/g], a formula was used that allows to calculate the content of the dye in the sorbent based on the model presented in [30]:

$$q = \frac{\left(t_i - \int_{t_0}^{t_i} f(t)dt\right) \cdot Q \cdot C_0}{m} \tag{2}$$

where: q - adsorbed dye [mg/g], Q - volumetric flow rate [dm^3/h], C_0 - initial concentration of the dye in the solution [mg/dm^3], m - adsorbent mass [g], t_i - successive time moment [h].

In this case the volumetric mass transfer coefficient or in-pellet diffusion coefficient are not required, unlike in the case of solving the mass-balance equation for the column.

All calculations required to determine dye concentration in the sorbent q [mg/g] were carried out using ORIGIN software with the following procedure employed: C/C_0 were graphed as a function of time and integrated. With the known integral values, the amount of dye adsorbed on the bed was calculated using the above model.

Interpretation of results

The results of experiments and calculations are presented in Figures 8 and 9.

Breakthrough curves are presented for various initial concentrations and four volumetric flow rates. Experiments were continued until inlet concentration equalled outlet concentration. Characteristic values were also marked which corresponded to the breakthrough and saturation concentration. For C_0 = 50 mg/dm^3 and for the lowest flow, sorption process lasted approximately 220 hours.

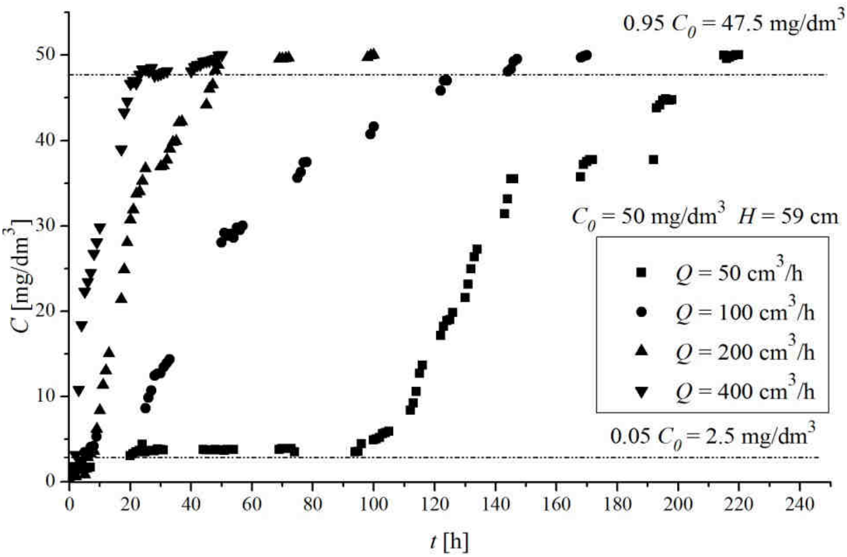

Fig. 8. Breakthrough curves for different volumetric flow rates

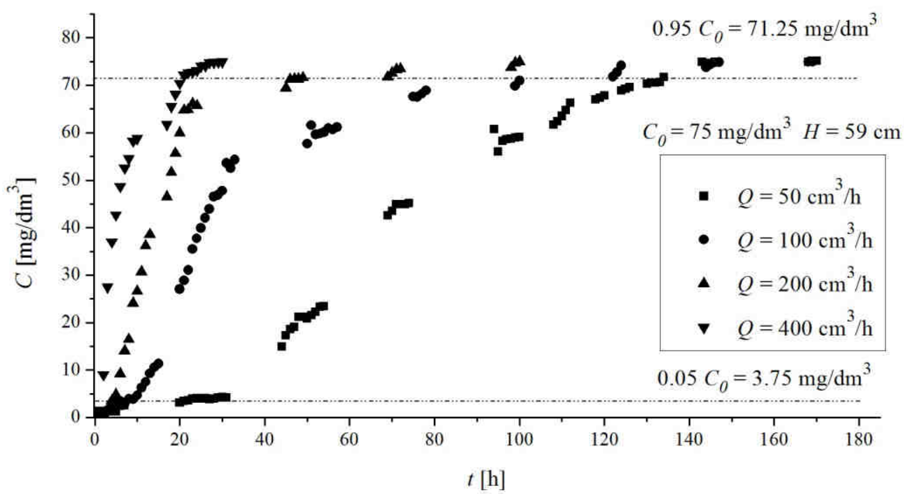

Fig. 9. Breakthrough curves for different volumetric flow rates

Figure 10 shows the impact of bed height on breakthrough and saturation time and the corresponding concentrations for selected process parameters.

Equation (2) was used to calculate the amount of the dye adsorbed onto corncobs. Figure 11 shows some of modelling results for C_0 = 75 mg/dm^3 and different volumetric flow rates. Figures 12 and 13 show (for different parameters) the change of bed exploitation within the range from 100 to 0% which correlates with the amount of adsorbed dye once the solution is discoloured.

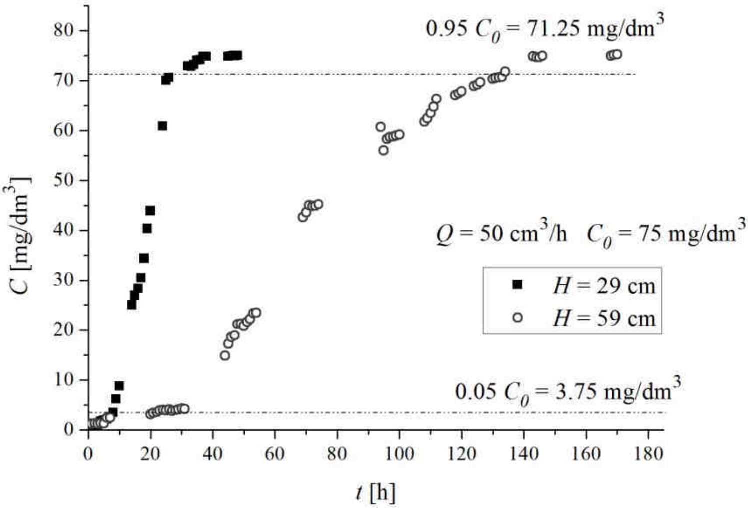

Fig. 10. Change of dye concentration with time in the column

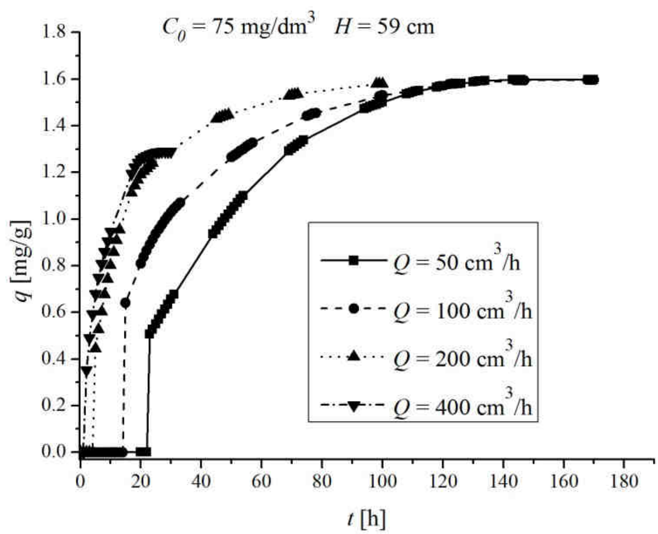

Fig. 11. Amount of dye adsorbed per sorbent unit mass with time

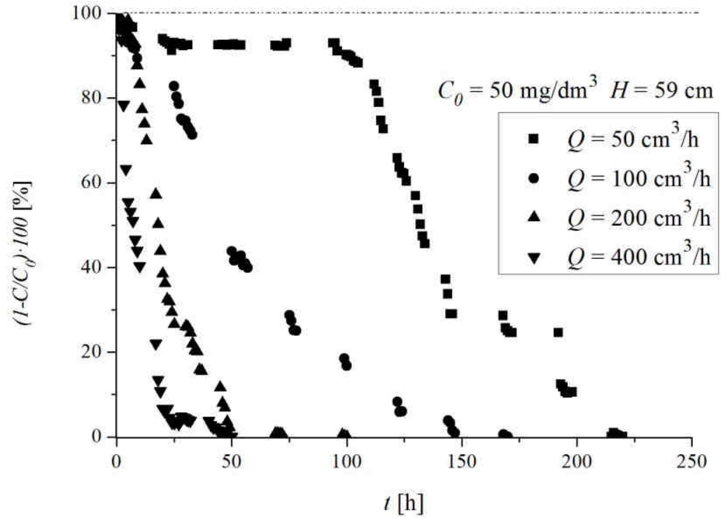

Fig. 12. Change of bed sorption capacity with time

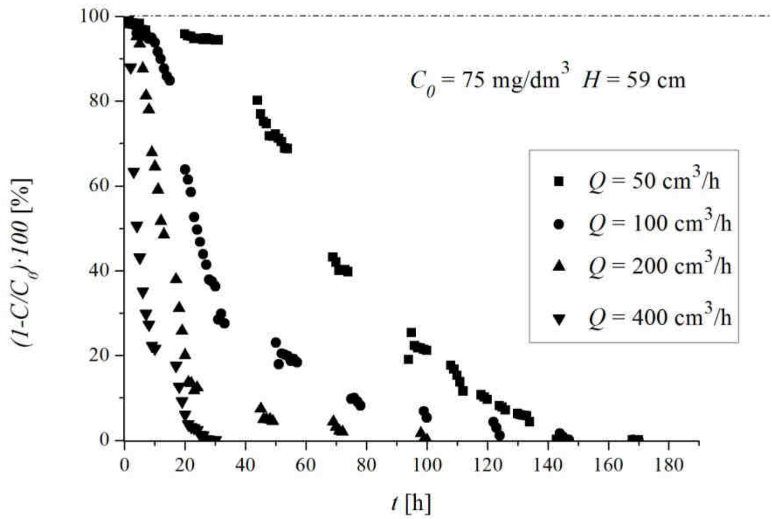

Fig. 13. Change of bed sorption capacity with time

Summary

The aim of the present paper was to determine sorption capacity of thermally and chemically pretreated granulated corncobs as a potential natural adsorbent to remove Direct Orange 26 azo dye from aqueous solutions. Based on literature reports it was assumed that corncobs, containing lignocellulosic complex, can adsorb dyes and other contaminants from aqueous solutions.

Sorption capacity was assessed in experiments with fixed bed column and varying process parameters. It was shown that initial concentration and volumetric flow rate of the dye solution have a major impact on the results obtained in the analysis. Higher values implied shorter breakthrough and saturation times. A similar relation was observed for smaller bed height.

For mathematical description *ie* to determine the amount of the dye retained by the sorbent, a simple but effective mathematical model was used. Additionally, the availability of sorbent for the dye was determined which changed over the time of the experiment.

Conclusions

The aim of the present paper was to determine sorption capacity of thermally and chemically pretreated granulated corncobs as a potential natural adsorbent to remove Direct Orange 26 azo dye from aqueous solutions. Based on literature reports it was assumed that corncobs, containing lignocellulosic complex, can adsorb dyes and other contaminants from aqueous solutions.

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