BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iași
Volumul 66 (70), Numărul 2, 2020
Secţia
CHIMIE şi INGINERIE CHIMICĂ

REACTIVE ARANCIO KEMAZOL 3R DYE REMOVAL FROM AQUEOUS SOLUTIONS BY ADSORPTION ONTO SAWDUST

BY

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Received: April 15, 2020
Accepted for publication: May 19, 2020

Abstract. The paper presents a few findings after some laboratory adsorption tests onto sawdust applied to retain the reactive Arancio Kemazol 3R dye from aqueous solutions by using the ‘batchwise’ sorption technique. For high efficiency of reactive dye removal, some operating parameters such as initial dye solution pH (2.5-10.86), dye concentration (13-60 mg/L), adsorbent concentration (3-80 g/L), temperature (5°, 20° and 40°C), and sorption time (0.5-24 h) were studied. The best adsorption performance was obtained at very high acidic pH (2.5-2.8), with sawdust concentration of 13-60 g/L, temperature of 5°C till 20°C, initial intermittent agitation (no more than 3-5 min), continuous sorption operating regime, a minimum contact time of 480 (pH=2.6), or 600 min (pH=5.40), and was varied between 54.77% (5°C, pH=2.6 and 60 g/L adsorbent) and 44.78% (20°C, pH=2.6 and 80 g/L adsorbent).

To increase the reactive dye removal must be applied other physical-chemical or biological treatment steps (*i.e.* coagulation-flocculation, advanced oxidation/reduction, membrane processes as ultrafiltration, ionic exchange, etc.) and obligatorily a neutralization step.

Keywords: adsorption; operating parameters; reactive dye removal; sawdust; treatment efficiency.

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1. Introduction

The municipal and industrial wastewaters can be commonly treated together, being sometimes advantageous, especially when the industrial wastewaters are in greater volumes than that which usually enter in urban municipal wastewaters. The existence of a single treatment plant can lead to reduction of treatment cost and an efficient cooperation between industry and populated center for wastewaters treatment. In addition, a single responsible staff of wastewaters treatment system for the entire populated center can lead to an increasing efficiency in exploitation, but sometimes the treatment in common of municipal and industrial wastewaters can be stopped due to existence of some inhibitory and toxic substances and/or suspended solids in the industrial wastewaters which must be eliminated in pre-treatment stations if it is wanted the common treatment of both municipal and industrial wastewaters.

The industrial wastewaters are produced after the industrial and/or process water used in preparation of raw materials, in the industrial technological processes or in other types of industrial and human demands/needs. The industrial wastewaters are characterized by great variations of concentrations and compositions, being necessary the homogenization and sometimes pre-treatment before discharge in centralized treatment plants. The organic component of industrial wastewaters varies qualitatively in restricted limits being relative constant when the same raw materials are used and the same types of technological products and services are processed. The complexity of organic pollutants increases greater and greater in industrial companies with diversified production, such as companies which produce colorants, drugs, fine synthesized organic products, etc. Some organic species existing in the industrial wastewaters are easily degraded by micro-organisms, others require a selected adaptable flora, or are resistant to micro-organisms action and must be eliminated or removed by advanced treatment methods.

One adequate advanced wastewater treatment system can be based on *adsorption* using non-polluted production wastes, thus being minimized and valorized efficiently a few certain categories of natural production wastes. Moreover, in this case, the required equipments/installations to be used for removal of polluting species is not complicated, being possible the use of existing ones adapted for adsorption treatment in open or closed systems with possible additional hydraulic loads.

The adsorption continues to be increasingly discussed in a lot of research reports, in which is considered that the corresponding mechanism depends on the effluent (wastewater) characteristics, the adsorbent characteristics, imposed restrictive limits of discharge in aquatic receptors and also the operating conditions, being possible to be based on *physical adsorption* (van der Waals, hydrogen or hydrophobic bonds, etc.), *chemiosorption* (*physical-chemical adsorption* due to weak physical bonds but also strong ionic exchange, covalent bonds) and *biosorption* (*biological adsorption* associated or not with other *physical-chemical processes* performed simultaneously, or consecutively in the same aquatic environment) with very good results in term of efficiency *vs.* costs and easily to be applied (Anjaneyulu *et al*., 2005; Doke and Khan, 2012; Gorduza *et al*., 2002; Gupta and Suhas, 2009; Gupta *et al*., 2009; Han *et al*., 2012; Hameed, 2008; Hubbe *et al*., 2012; Shih, 2012).

A natural woody adsorbent which can be applied in adsorptive treatments of different industrial effluents is the *sawdust* that can be used for different polluting species removal (*e.g*., colorants, reactive dyes, phenol and its derivates) (Zaharia, 2015) especially for low industrial effluent flows.

This paper summarizes a few experimental findings performed to evaluate the adsorptive potential of sawdust (production woody waste) especially for Arancio Kemazol 3R dye (reactive textile dye) removal (%) from aqueous systems. The influence of a few operating parameters on the dye sorption efficiency onto sawdust, *i.e.* initial pH, reactive dye concentration, adsorbent concentration, temperature and adsorption time, was mainly had in view and the best operating conditions for highest dye removal proposed.

2. Experimental

2.1. Materials and Reagents

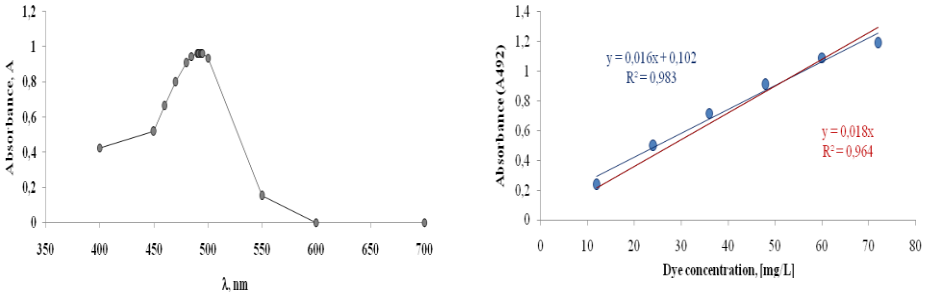
Reagents: Arancio Kemazol 3R dye (reactive textile dye) as reference model of organic persistent present in different industrial effluents, or receiving water resources. Working dye solutions were prepared by appropriate dilution with distilled water of a stock solution, *i.e.* 600 mg of Arancio Kemazol 3R/L of solution. Other reagents were sodium hydroxide ($NaOH$; Chemical Company, Iaşi, Romania) of 0.1N and hydrochloric acid (concentrated HCl; Chemical Company, Iaşi, Romania) of 0.1N, used for pH adjustment. All reagents were of analytical purity.

Adsorptive material: *Romanian sawdust*, as production waste (resulted from conifer wood processing), dried in air and sieved to obtain fractions between 1-2 mm. The *principal constituents* of sawdust are *cellulose*, *lignin* and *hemicellulose*, whilst chemical composition of conifer wood was of 49.9% C, 6.4% H, 43.0% O and 1.0% N, and caloric power of 2035 kcal/kg (Şuteu *et al*., 2009, 2012; Zaharia and Şuteu, 2012; Zaharia *et al*., 2012).

2.2. Analysis Methods

Dye content determination. The wavelength for maximum absorbance (λ_{max}) and the calibration curve of Arancio Kemazon 3R dye in aqueous solution were established. Thus, the absorbance measurements for dye concentration determination were firstly performed with a known dye concentration (24 mg of Arancio Kemazol RB dye /L of aqueous solution) in range of 400 nm until 700 nm for finding the λ_{max} (Fig. 1*a*), and after only at 492 nm for the reactive dye calibration curve establishment (Fig. 1*b*). Laboratory equipment available to carry out these measurements was VIS SP 830 Plus 1.06 spectophotometer (MeterTech Co.), being used for gravimetric measurement a Partener WPS 510/2/C digital balance.

PH measurement. It was done directly at a Combo pH/EC/TDS Testers HANNA Instruments.



a *b*

Fig. 1 – *a*) Vis Spectra of Arancio Kemazol 3R dye solution (λ_{max} = 492 nm); *b*) Calibration curve of Arancio Kemazol 3R dye solution.

2.3. Adsorption Working Methodology

The adsorption experiments were performed using ‘batchwise’ technique at laboratory scale setup. A variable amount of sawdust (0.075 – 2 g per 25 mL of sample) was placed in each conical flask (100 mL), at different temperatures (5°C, 20°C and 40°C) controlled with a thermostated assembly and analized after a certain period of time (*t*, min; at least 0.5-20 h), or 24 h when the sorption equilibrium was always attained.

The adjustment of textile effluent pH was done with HCl 0.1 N or NaOH 0.1 N.

After a corresponding adsorption time (*t*) and/or 24 h, the dye content in the supernatant was determined after the adsorbent separation by sedimentation.

The dye removal, or treatment degree for reactive dye was calculated with the relation (1):

$$R(\%) = \frac{C_0 - C_t}{C_0} \cdot 100 \qquad (1)$$

where: C_0 and C_t are the initial and residual (after *t* adsorption time) dye concentration in supernatant [mg/L, or A_{492} value].

3. Results and Discussion

In previous reports were established a few principal operating parameters that must be had in view for the adsorption/sorption/biosorption process of different organic species onto adsorptive materials, especially ‘low cost’ adsorptive materials (Zaharia, 2015, 2016, 2018, 2019; Zaharia and Şuteu, 2012; Zaharia *et al*., 2012).

In this study it was proposed the admissible variation field for a few operating parameters such as initial solution pH, dye concentration, adsorbent concentration, temperature, and contact time, considered with significant influence on the adsorption process of studied reactive dye onto sawdust, and determined the highest efficiencies in reactive dye removal (Grădinaru, 2020).

3.1. The Influence of Initial pH in Dye Adsorption onto Sawdust

Series of experiments were performed at different pH values on aqueous solution with 60 mg of reactive dye /L of aqueous solution using a dose of 50 g of sawdust/L (1.25 g of adsorbent / 25 mL of sample). The results are presented in the Fig. 2.

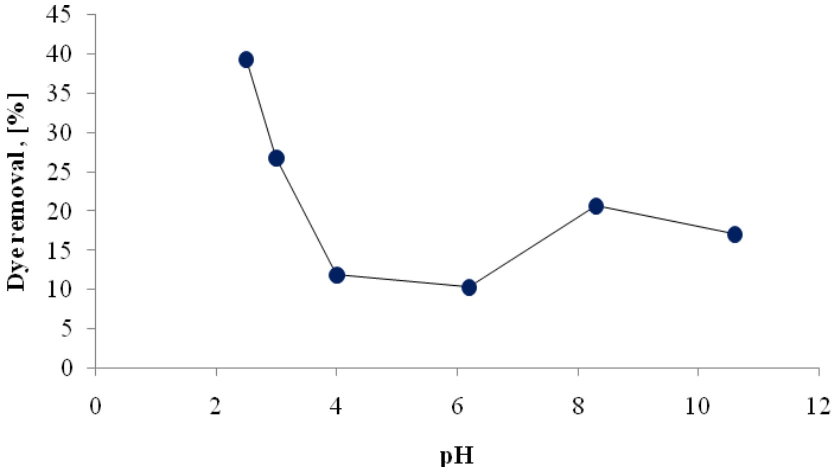


Fig. 2 – Influence of pH on dye retention by adsorption onto sawdust (50 mg/L dye; 50 g of adsorbent /L; room temperature and 21 h of adsorption).

As can be seen in the Fig. 2, the retention of reactive dye in acidic aqueous environment is higher related to other extreme, neutral or basic pH. The maximum retention of 39.388% is achieved at very high acidic pH 2.50 at room temperature and minimum of 10.313% at pH 6.20 for a 50 mg/L dye concentration.

3.2. The Influence of Dye Concentration in Dye Adsorption onto Sawdust

A first series of adsorption tests were performed at pH=5.40 (Fig. 3) by using relative small amounts of sawdust (3 g of adsorbent/L of dye solution, meaning 0.075 g of sawdust/ 25 mL of dye solution) for different dye concentrations, but the results were not satisfactory indicating that the tested adsorbent amount was not enough for removal of this reactive dye from aqueous solution (no significant dye retention). Therefore, in the next series of experimental tests at pH=5.40, it was increased the sawdust doses used.

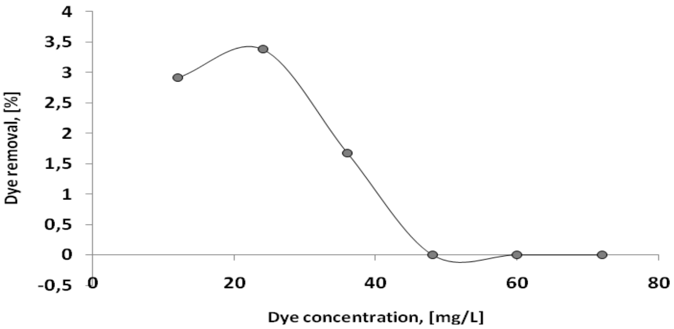


Fig. 3 – Dye removal *vs.* dye concentration (pH=5.40; 3 g/L of adsorbent; 22 h of adsorption).

In the Fig. 4, it is summarized the experimental results performed with 4 g of adsorbent/L (0.1 g of sawdust / 25 mL of sample) at pH=5.40, noting that for dye concentrations exceeding 40 mg/L, the dye removal (dye retention) was low (minimum dye removal = 1.673%; maximum dye removal = 3.386%) fact that is explainable by the possible elimination of colored phenolic derivates from the lignocellulosic-based structure of adsorbent matrix (sawdust).

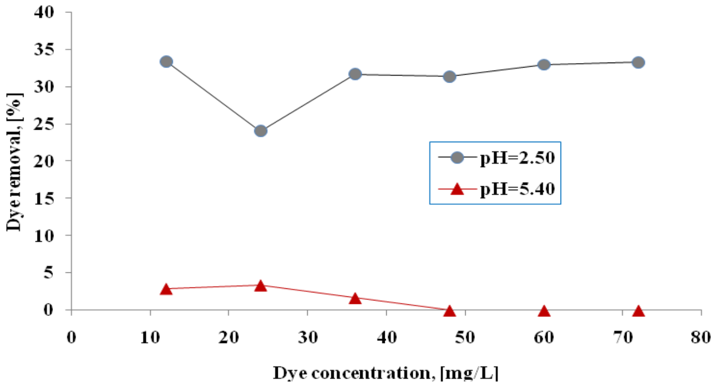


Fig. 4 – Dye concentration influence on dye adsorption onto sawdust
(pH =2.50 and 5.40; 60 g/L of adsorbent; room temperature and 22 h of adsorption).

At very high acidic pH (pH=2.50), the dye removal (%) increases as shown in the Fig. 4 related to very low or almost zero values performed at pH=5.40. Thus, the maximum dye retention at pH=2.50 was 33.456% for 12 mg/L of dye and minimum 24.089% for 24 mg/L of dye.

3.3. The Influence of Adsorbent Concentration in Dye Adsorption onto Sawdust

The influence of adsorbent dose was studied at different pH values. The results obtained at pH=5.40 and also pH=2.50 are presented in Fig. 5.

It is clearly visible (Fig. 5) that the dye retention is increasing with the added amount of adsorbent (sawdust). The testings were performed with 60 mg/L of dye, obtaining maximum dye retention (20.222%) working with 2 g of sawdust/25 mL of sample (80 g/L of adsorbent) and minimum (2.972%) working with 0.35 g/25 mL of sample (14 g/L of adsorbent) at pH=5.40. Higher removals were obtained at pH=2.50, corresponding to a maximum of 39.572% working with 80 g/L of adsorbent and a minimum of 26% working with 14 g/L of adsorbent.

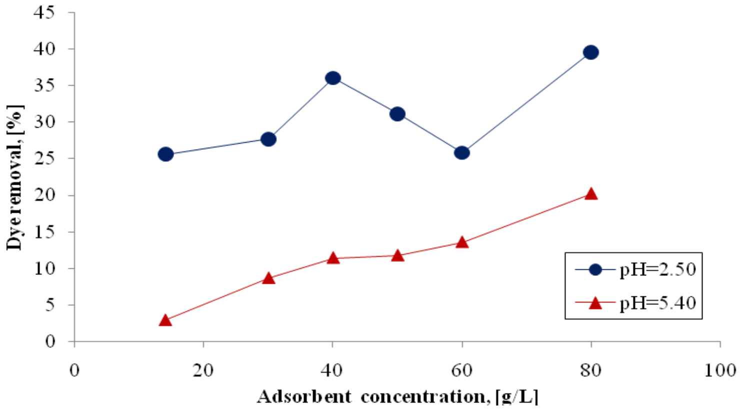
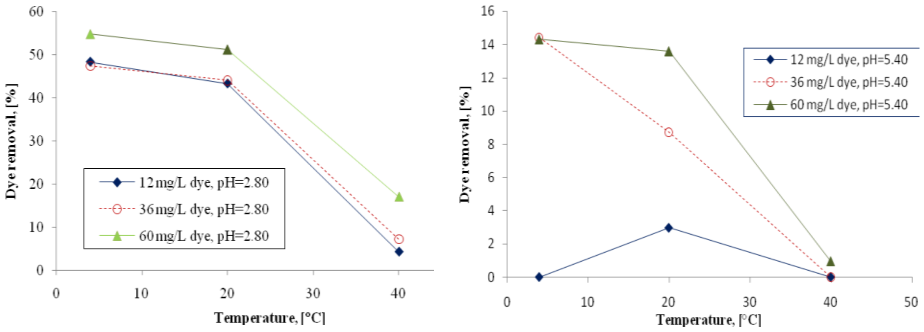


Fig. 5 – Influence of adsorbent concentration on dye adsorption
(60 mg/L of dye; pH 5.4 and pH 2.80; room temperature and 22 h of adsorption).

At very high acidic aqueous dye solution, the variation of dye removal is not constantly increasing with the adsorbent concentration probably due to elimination of colored phenolic compounds from the solid adsorbent matrice which increases the value of solution absorbance at 492 nm. Comparing obtained results (Fig. 5) can be concluded that acidic pH is most favorable for retention of this reactive dye. As the amount of sawdust increases the reactive dye retention is increasing, with maximum value of 39.571% and minimum value of 25.581%.

3.4. The Influence of Temperature in Dye Adsorption onto Sawdust

Series of adsorption experiments were performed at two pH values (*i.e.* pH=5.40 and very high acid aqueous solution of pH=2.80) working with three different dye concentrations (12, 36 and 60 mg of dye /L) at three different temperature, *i.e.* 4°, 20° and 40°C using adsorbent doses of 50 g/L (*i.e.* 1.25 g of adsorbent/25 mL of solution sample). The results are illustrated in Fig. 6.



a *b*

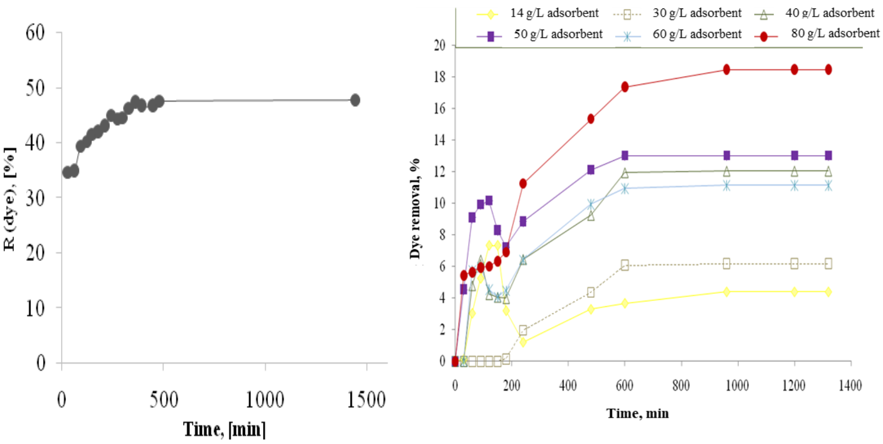
Fig. 6 – Influence of temperature in dye adsorption onto sawdust (pH=2.80 and 5.40; C_{dye}= 12, 36 and 60 mg of dye/L; 50 g of adsorbent/L and 21 h of adsorption).

As shown in Fig. 6, the best efficiencies in the reactive dye adsorption were obtained in very acidic aqueous environment (pH=2.80) at low temperature (5°C), the maximum dye removal being of 54.77% when it worked with a relative high concentration of dye (60 mg of dye/L) and 48.288% or 47.348% for lower dye concentrations of 12 or 36 mg of dye/L, respectively. The lowest value of dye removal was performed at the highest temperature (40°C), being no more than 17.11% when worked with concentration of 60 mg of dye/L, or 4.305% at dye concentration of 12 mg of dye/L. Moreover, the best result of dye removal at low temperature (4°C till 20°C) indicates a possible spontaneous exothermic mechanism of dye adsorption onto sawdust.

At pH=5.40, no more than 1% for dye removal was obtained and the only logical explanation is the accumulation of colored compounds due to thermal decomposition of natural adsorbent at high temperature.

3.5. The Influence of Adsorption Time in Dye Adsorption onto Sawdust

Series of experiments were performed at pH=5.40 and pH=2.80 working with a dye concentration of 60 mg/L, at room temperature (*i.e.* 18°-20°C) using different concentrations of adsorbent (14, 30, 40, 50, 60 and 80 g of adsorbent /L). The results are presented in Fig. 7.



a – pH=2.60 and 50 g/L adsorbent *b* – pH=5.40 and different adsorbent doses

Fig. 7 – Influence of adsorption time onto dye removal onto sawdust (60 mg of dye/L and room temperature). (*a*) pH=2.60 and $C_{sorbent}$=50 g of adsorbent/L; (*b*) pH=5.40 and different adsorbent doses.

One of the most important factors in reactive dye adsorption experiment onto sawdust is the adsorption time or contact time between adsorbent and aqueous dye-containing solution, therefore dye concentration measurements at every 30 min were performed for appreciation of adsorption performance. As shown in Fig. 7, the adsorption equilibrium was attained after almost 480 min of sorption and maintained at the same value till 1440 min and even more at very acidic aqueous environment (pH=2.60), the maximum value of dye removal being of 47.833%. At pH of 5.40, the sorption equilibrium was attained after a higher value of adsorption time, meaning more than 600 min, the maximum dye removal being of 18.47% working with 80 g adsorbent/L and minimum 4.394% with 14 g adsorbent/L.

4. Conclusions

1. A few laboratory scale set-up adsorption tests applied for reactive dye (Arancio Kemazol 3R) solutions were performed for finding the operating conditions for highest dye removals onto sawdust. *Sawdust* is considered as an abundant and inexpensive material due to rapid development of wood processing industry around the world, being easy to find and having the necessary properties to be used for treatment of wastewater/water contaminated with different colored species such as reactive dyes, oil etc.

2. The reactive dye adsorption is dependent of a few operating parameters such as initial solution pH, adsorbent concentration, dye concentration, temperature and sorption time. The best pH value for this

reactive dye removal is found at very high acidic pH (2.5-2.8). The reactive dye removal increased with the increasing of adsorbent dose (sawdust).

3. The adsorption equilibrium at very acid (pH=2.5-2.8) or low acidic (pH=5.4) pH attained after 480 or 600 min, respectively. The adsorption performance was studied also for different adsorption operating parameters for around 24 h of adsorption.

4. Reactive dye removal is better at low temperature (around 5°C) possibly due to an exothermic adsorption process.

5. The highest value of reactive dye removal was of around 54.77% after 24 h of continuous sorption into static regime at pH of 2.80 and temperature of 5°C, for other continuing treatments is necessary a neutralization step.

6. These adsorption tests suggested that sawdust can be used as natural alternative adsorbent for reactive dye removal. The tests will continue with others for elucidation of adsorption mechanism type and adsorption behavior at different external pressures and load variations, but also with modeling and optimization of adsorption onto sawdust applied for reactive dye-containing aqueous environments.

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REȚINEREA COLORANTULUI REACTIV ARANCIO KEMAZOL 3R DIN SOLUȚII APOASE PRIN ADSORBȚIE PE RUMEGUȘ

(Rezumat)

Lucrarea prezintă câteva informații găsite în urma unor teste de adsorbție în laborator pe rumeguș aplicate pentru reținerea colorantului reactiv Arancio Kemazol 3R din soluții apoase folosind tehnica adsorbției în regim static. Pentru obținerea unei eficiențe ridicate de îndepărtare a colorantului reactiv au fost studiați câțiva parametri

operaționali: pH-ul (2,5 - 10,86), concentrația colorantului (13 - 60 mg/L), concentrația de adsorbant (3 - 80 g/L), temperatura (5°, 20° și 40°C) și timpul de adsorbție (0,5 - 24 ore).

Cea mai bună performanță a fost obținută la pH foarte puternic acid (pH 2,5 - 2,8), cu o concentrație de rumeguș 13 - 80 g/L, la temperatura de 5°C până la 20°C, cu agitare intermitentă inițială (nu mai mult de 3 - 5 min), în regim continuu de operare, timp de contact minim de 480 (pH=2,6) sau 600 min (pH=5,40) și a variat între 54,77% (5°C, pH=2,6 și 60 g/L adsorbant) și 44,78% (20°C, pH=2,6 și 80 g/L adsorbant).

Pentru mărirea gradului de îndepărtare a colorantului reactiv trebuie aplicate alte trepte fizico-chimice sau biologice de epurare (*i.e.* coagulare-floculare, oxidare/reducere avansată, procese de membrană precum ultrafiltrarea, schimbul ionic, etc.) și obligatoriu o treaptă de neutralizare.