

Sorption of chromium complex dye on activated carbon and neutral polymeric adsorbent

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The sorption behavior of the anionic chromium complex dye Lanasyn Navy M-DNL from aqueous solution onto activated carbon Norit RB 08.CC (AC) and, as an alternative, the neutral polymeric adsorbent Macronet MN 200 (MN 200) was investigated under various experimental conditions. The sorption properties of both adsorbents depend on their surface functional groups and the electrical charge of the surface net. The adsorption capacity of the polymeric adsorbent MN 200 for the chromium complex dye was found to be relatively higher than that for AC in both acidic and neutral solutions. At the dye solution concentration of 4–80 µmol/l, pH 2 and temperature 293 K, the maximum Langmuir adsorption capacity on AC and MN 200 was found to be 2.46 µmol/g and 3.88 µmol/g, respectively. The sorption capacity for AC and MN 200 strongly depends on solution pH, with higher values at acidic pH. With increasing the solution temperatures from 297 K to 333 K, the sorption capacity for AC decreases and for MN 200 increases. The experimental data showed a good correlation with the Langmuir and Freundlich isotherms models. Using both adsorbents at pH 2, the maximum removal of chromium ions (residual concentration below 1.5 mg/l) and organics (values of chemical oxygen demand below 100 mgO₂/l) was obtained when the initial concentration of chromium and organic compounds in dye solution was below 6.16 mg/l and 735 mgO₂/l, respectively.

The Macronet MN 200 could be employed as an alternative to commercial activated carbon in the removal of metal complex anionic dye from wastewater.

Key words: chromium complex dye, basic activated carbon, hypercrosslinked polystyrene, sorption

INTRODUCTION

Improper treatment and disposal of dye-contaminated wastewaters from textile, dyeing, ink, and related industries have provoked serious environmental concerns all over the world [1]. The textile finishing industry, as a major user and potential polluter of water, is under particular pressure to reduce water consumption on both environmental and economic grounds. Wastewater from textile industries is highly coloured, complex and variable in nature depending upon the fiber processed as well as on the associated dyestuffs and auxiliary chemicals employed [2–5]. One problematic group of substances present in mixed wastewater from textile industry, which must be removed, is metal complex dyes [6]. Metal complexes can be found in textile finishing wastewater when using acid, direct, and reactive dyes, as well as pigments [7, 8]. Metals used in dyes include mainly chromium, cobalt and

copper. Environmental concerns arise from the carcinogenic properties of these metals and from amines formed by the reductive cleavage of azo groups [9]. Therefore, removal of metal complex dyes before wastewater disposal is necessary. However, only a limited number of studies including coagulation, chemical degradation, adsorption using fly ash, pine sawdust, deacetylated chitin on the removal of metal complex dyes has been found in the literature [10–13].

Dyes are normally present in textile wastewater at a concentration of 10–50 mg/l; however, the colour has been noted above 1 mg/l [14]. Different biological, chemical and physical methods can be used to treat dye wastewaters [15]. Although chemical and biological methods are effective for removing dyes, they require specialized equipment and are usually quite energy intensive; in addition, large amounts of by-products are often generated. The physical methods, which include adsorption, ion exchange and membrane filtration, are effective for removing dyes without producing unwanted by-products, recovering water for reuse and

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preventing contamination of the environment by carcinogenic metal ions and azo compounds. Activated carbon is widely used as an adsorbent due to its high surface area and high adsorption capacity. Adsorption on activated carbon of cationic and anionic dyes, acid and reactive dyes has been investigated by a number of researchers [5, 16–20]. There are some disadvantages in using activated carbon, e. g., high regeneration costs and production of fines due to their brittle nature [21]. For this reason, many researchers have investigated, on the one hand, low-cost, locally available substitutes for activated carbon, made from natural sources such as clays, zeolite, montmorillonite, smectite, bentonite, sepiolite to remove dyes from wastewater [22]. On the other hand, as the adsorption capacity of the above adsorbents is not high, new adsorbents, including polymeric ones, are still under development. Among the widely used polymeric adsorbents there is a class of neutral-to-weakly-polar-macroporous polystyrene resins synthesized using styrene-divinylbenzene. Synthetic porous polymeric sorbents are superb adsorbents for organic compounds and, because of their higher physicochemical stabilities and better regeneration properties, have been commercialized as alternatives to activated carbon for adsorption-oriented applications [23]. Resin-based adsorption technologies have been successfully developed for removing organic pollutants from industrial effluents such as dye wastewaters [24]. It is generally accepted that porous structures, specific surface areas and surface properties of resins together determine adsorption. The van der Waals forces, in particular the π - π interactions between the aromatic rings of resins and adsorbate, are thought to be the primary driving force for adsorption [25].

Macroporous neutral resins such as OC1064, OC1066 (Bayer AG, FR Germany) showed moderate maximum loadings of reactive dyes (100–400 $\mu\text{mol g}^{-1}$ or 100–400 mg g^{-1}) but a low affinity and were not suitable for large dyes ($>1000 \text{ g mol}^{-1}$) [26]. The neutral hypercrosslinked polystyrene Macronet MN 200 produced by Purolite International Ltd. is characterized by a very high internal surface area ($>1000 \text{ m}^2 \text{ g}^{-1}$) that approaching those of activated carbons [21]. It is particularly suitable for the sorption of organic substances, especially those having a high molecular weight and lipophilic properties, for the separation and determination of inorganic anions and metal cations [27]. So far, there has been no report in the literature on a study of metal complex dye adsorption using neutral hypercrosslinked polystyrene MN 200 as a sorbent.

In this study, the removal of chromium complex dye from water has been investigated using two adsorbents: commercial activated carbon and neutral hypercrosslinked polystyrene Macronet MN 200 as an alternative. The physical and chemical characteristics of the sorbents, including the point of zero charge (pH_{pzc}) and surface functional groups, were determined using standard analytical procedures. Adsorption isotherms, thermodynamic characteristics for chromium complex dye sorption were determined.

EXPERIMENTAL

Materials

Granular activated carbon Norit RB 0.8 CC (AC) was purchased from the Norit Company (AC Amersfoort, the Netherlands). The total surface area (B. E. T.), iodine number and apparent density of the adsorbent were 1150 m^2/g , 1100 and 0.51 g/ml , respectively (obtained from the manufacturer).

Macronet MN 200 was supplied by Purolite International Ltd. It is a neutral, macroporous polystyrene crosslinked with divinylbenzene, pore volume 1.1 ml/g , specific gravity 1.04 g/ml , inner surface area 1000 m^2/g (obtained from the manufacturer).

The sorbents were washed with deionized water and then dried at 60 °C for 12 h.

The chromium complex dye was the commercial textile dye anionic Lanasyne Navy M-DNL (1 : 2 chromium monoazo complex (trisodium bis[3-hydroxy-[(2-hydroxy-1-naphthyl)azo]naphthalene-1-sulphonato(3-)]chromate(3-)), molecular mass 834 g/mol , λ_{max} 616 nm). It was obtained from Clariant Producte AG (Switzerland). An accurately weighed quantity of the dye was dissolved in deionized water to prepare the stock solution. Experimental solutions of desired concentrations were obtained by successive dilutions.

Material characterization

The Boehm method, which is widely used for determination of acidic and basic surface groups of activated carbons, was used to characterize activated carbon as well as Macronet MN 200 [28]. Prior to determination, the sorbent samples were washed with 0.1 N HCl followed by deionized water. Each sample (1,000 g) was accurately weighed and mixed with 50 ml of 0.05 N solution of Na_2CO_3 , NaHCO_3 , NaOH, or HCl in 100-ml conic flasks; the suspensions were shaken for 3 days. The excess base and acid in the filtrate was titrated with 0.1 N HCl or NaOH. Surface acidity and basicity were calculated on the basis of the assumption that NaHCO_3 neutralizes carboxyl groups only, Na_2CO_3 neutralizes carboxyl and lactonic groups, NaOH neutralizes all acidic groups, including phenolic groups, and HCl neutralizes all basic groups.

The point of zero charge (pH_{pzc}) was measured to investigate the total surface charge for the adsorbents according to the method described in [29]. A mixture of 100 mg of adsorbent and 50 ml of 0.1 M KNO_3 solution was agitated at 20 °C for 24 h until the equilibrium state. The initial pH of 0.1 M KNO_3 solution was changed from 1.5 to 10, using 0.1 M HNO_3 and 0.1 M KOH. When the equilibrium solution pH did not change with increasing the initial pH, the constant pH value was considered to be the point of zero charge (pH_{pzc}) for the adsorbent. At a solution pH lower than pH_{pzc} , the total surface charge will be on average positive, whereas at a higher solution pH it will be negative. The equilibrium solution pH was measured with a pH 211 meter (Hanna Instruments). All chemicals used in the study were of reagent grade.

The surface morphology of the adsorbents was measured by scanning electron microscopy (SEM). The microscope used was EVO 50EP (Carl Zeiss SMT AG), equipped with energy and wave dispersive X-ray spectrometers (Oxford Instruments) and a secondary electron detector (low vacuum mode, 10 kV, 50 Pa, working distance 10 mm).

Adsorption experiments

The sorption of dye onto activated carbon or MN 200 was studied in batch experiments by mixing 0.5 g of sorbent with 25 ml of a given initial concentration aqueous dye solution. The dye solutions were prepared by dissolving appropriate amounts of material in distilled water. The concentration of the dye solution in the series ranged from 4 to $80 \cdot 10^{-3}$ mmol/l. The pH values of initial solutions were measured and adjusted with 0.1 M HCl or 0.1 M NaOH. After sorption, they were rechecked, and the change (decrease or increase) in solution pH was determined in the case of activated carbon. Preliminary kinetic experiments were completed to establish the time required for the sorption system to reach an equilibrium. The sorption of the dye on both activated carbon and MN 200 was relatively fast, and one day was needed to attain the equilibrium. After one day, the samples were centrifuged and the residual concentration of dye was ascertained with a UV-Vis Spectrometer Cintra 101 (GBS Scientific Equipment (USA) LLS) at a respective $\lambda_{\max}$ value which is 616 nm for this dye. The dye concentration was calculated from the calibration curve.

The residual colour, Res (%), was calculated by comparing the absorption (A) of a treated sample with a reference treated identically, but without sorbent:

$$Res (\%) = A (\text{sample}) \cdot 100\% / A (\text{reference}). \quad (1)$$

This was necessary because the molar extinction coefficient of the dyes changes with pH.

Residual concentrations were calculated by multiplying the residual colour with the original concentration:

$$C = Res \cdot C_0, \quad (2)$$

where C_0 (mmol/l) is the initial concentration and C (mmol/l) the residual concentration of the dye.

The dye distribution coefficients (K_d) were calculated as

$$K_d = (C_0 - C_e) V / C_e m, \quad (3)$$

where (C_e) is the dye concentration at equilibrium, V is the volume of the solution, ml, and m is the mass of the sorbent, g.

The sorption capacity of the sorbent (q_e , mmol/g) was calculated:

$$q_e = (C_0 - C_e) V / m. \quad (4)$$

The chemical oxygen demand (COD) values of the dye solutions were determined using a Spectroquant TR 320 – Spectroquant Picco analyser.

The concentration of chromium was determined using atomic adsorption spectrometry (Perkin–Elmer 603).

RESULTS AND DISCUSSION

Adsorbent surface acidity / basicity

Oxygen-containing functional groups (e. g., carbonyl / carboxyl and hydroxyl) are commonly present on the surface of sorbents such as activated carbon through the reactions with air [30]. They are also expected to be present on the surface of synthetic resins [31]. Surface functionality plays an important role in determining the adsorptive power of adsorbents. The functional groups possess an apparent surface acidity / basicity. The surface acidity and basicity of activated carbon and Macronet MN 200 measured by the Boehm titration are presented in Table 1.

Activated carbon displayed a low acidity (0.03 mmol/g) but a high basicity (0.5 mmol/g), while neutral Macronet MN 200 showed a total acidity six times higher than that of activated carbon contributed by phenolic groups.

Depending on solution pH, the protonation and deprotonation of surface functional groups create an electrical charge and hence a potential on the surface of adsorbents, which may further facilitate or complicate the adsorption of chromium complex dye [30, 32]. The activated carbon and Macronet MN 200 total surface charges measured as the point of zero charge (pH_{pzc}) are presented in Table 1. The pH_{pzc} is determined comprehensively by all the functional groups. In reference to activated basic carbon with a pH_{pzc} 9.95, neutral Macronet MN 200 showed a pH_{pzc} lower by about 6.35 pH units (pH_{pzc} 3.60). These results are in line with the Boehm titration. It was apparently due to a much higher acidity, in particular to phenolic group concentration, of the Macronet MN 200 as compared to the activated carbon (Table 1).

The net surface charge of MN 200 had been previously quantified by determining the zeta potential using a Zetmaster from Malvern Instruments and referred to in the literature [27]. At a pH less than 4.3, the presence of a significant positive zeta potential on the MN 200 surface was attributed only to the presence of oxygen in the framework of this sorbent. The anion adsorption properties (electrostatic

Table 1. Surface acidity / basicity of activated carbon Norit RB 08.CC and Macronet MN 200

Adsorbent	Phenolic groups (mmol/g)	Acidity (mmol/g)	Basicity (mmol/g)	Total (mmol/g)	pH_{pzc}
Norit RB 08.CC	0.03	0.03	0.5	0.53	9.95
Macronet MN 200	0.2	0.2	0	0.2	3.60

interaction) at pH less than 4.3 for this 'so-called' neutral sorbent were attributed to the following possibilities: $>C = \dot{O}H \leftrightarrow \dot{C} - OH \leftrightarrow$ delocalised charge in the whole polymer framework.

Dye sorption on activated basic carbons follows two parallel mechanisms, one involving dispersive interactions and the other electrostatic interactions [16]. The activated basic carbons are characterized by a high content of electron-rich sites on the surface and a low concentration of electron-withdrawing groups. The interaction of the dye molecules and the activated carbon surface is expected to occur between the delocalized π electrons of the oxygen-free Lewis basic sites and the free electrons of the dye molecule present in the aromatic rings and multiple bonds. The oxygen-free carbon sites can adsorb protons from the solution, offering a positively charged surface to the carbon. Thus, it is possible that negatively charged ions of the dye interact with these sites.

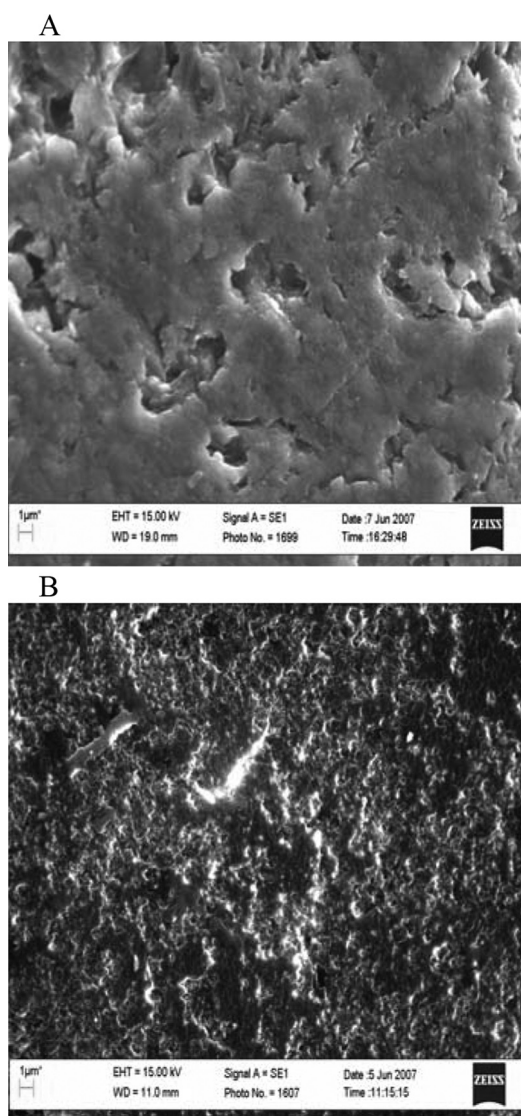


Fig. 1. Scanning electron micrographs of the cross-section of the activated carbon Norit RB 0.8 CC particle (A) and Macronet MN 200 bead (B) at 10000 $\times$ magnification

Surface morphology of the sorbents

Scanning electron microscopy examination results of the activated carbon Norit RB 0.8 CC particle and Macronet MN 200 bead is presented in Fig. 1.

In the SEM micrograph, the size of large pores in activated carbon is 1–2 μm (Fig. 1A). The surface texture of Macronet MN 200 is seen at a 10000 $\times$ magnification. Macronet MN 200 shows a uniform globular structure. The globule diameter is approximately 300 nm, thus creating mezo and macro pores (50–200 nm) enabling a rapid diffusion of dye molecules (Fig. 1B). Similar results for Macronet MN 200 were reported in [33].

Effect of initial solution concentration and pH on the colour removal

The effect of solution concentration and pH on dye removal from solution was studied under conditions identical for both activated carbon and Macronet MN 200. The values of the initial dye solution concentration ranged from 4 to 80 $\cdot 10^{-3}$ mmol/l, whereas the pH values of 2 and pH 7 were adjusted by dropping solutions of 0.1 M HCl or 0.1 M NaOH. The dependence of the residual colour of a solution ($Res, \%$) and the distribution coefficient of the dye (K_d) on an increase of the initial dye solution concentration and pH are presented in Fig. 2 and Fig. 3, respectively, which indicate that the removal of the dye is more effective at pH 2 than at pH 7 for both activated carbon and Macronet MN 200. While dye removal by Macronet MN 200 in identical conditions is more effective than that for activated carbon (e. g., for Macronet MN 200 the residual colour at pH 2 and with increasing the initial concentration from 4 to 80 $\cdot 10^{-3}$ mmol/l was obtained below 10%, however, for activated carbon, the residual colour increased from 10% to 60% with an increase of the initial concentration). At pH 2, the K_d values for Macronet MN 200 were about ten times as large as compared with the values

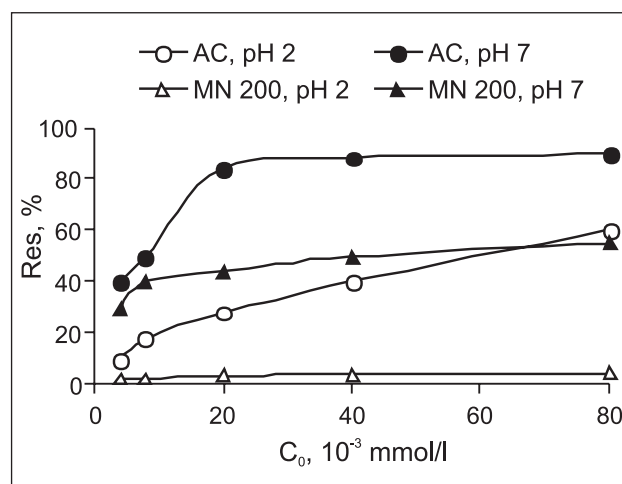


Fig. 2. Initial solution concentration and pH effects on the residual colour ($Res, \%$) for dye sorption onto activated carbon Norit RB 08 CC (AC) and Macronet MN 200 (conditions: adsorbent mass 0.5 g, volume of solution 25 ml; temperature 293 K)

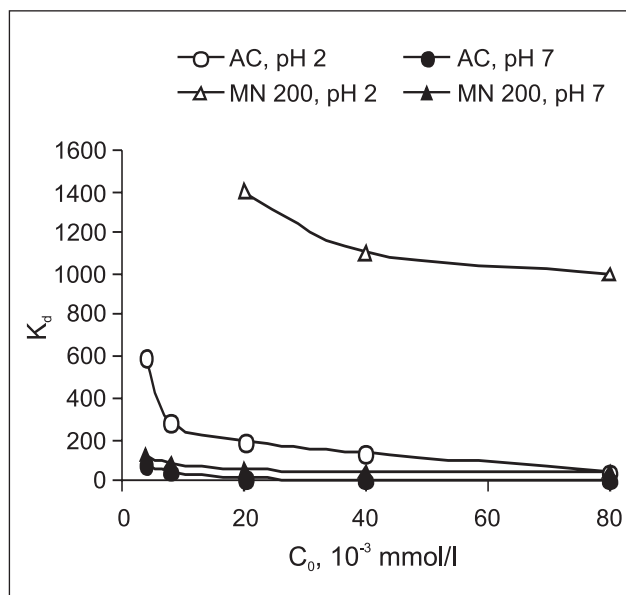


Fig. 3. Effect of initial solution concentration and pH on the distribution coefficient (K_d) for activated carbon Norit RB 08.CC (AC) and Macronet MN 200 (conditions: adsorbent mass 0.5 g, volume of solution 25 ml, temperature 293 K)

obtained for activated carbon (Fig. 3). This can be attributed to the different structure and nature of these two adsorbents: for the removal of anionic dye, the hypercrosslinked matrix and surface acidity of MN 200 are more favourable than the surface basicity of activated carbon.

With this commercial dye used, the indexes of dye solutions treated with activated carbon were compared with those of solutions treated using Macronet MN 200. Variations in the removal of hazardous components such as chromium and organic substances, including azo compounds (chemical oxygen demand (COD) at various pH and initial concentrations), are shown in Table 2 which shows that using both adsorbents, at pH 2 the maximum removal of chromium (residual concentration below 1.5 mg/l) and organics (the values of chemical oxygen demand below 100 mgO₂/l) is observed when the initial concentration of chromium and organic compounds is below 6.16 mg/l and 735 mgO₂/l, respectively.

Equilibrium isotherms

The data on dye adsorption on activated carbon and Macronet MN 200, obtained at the initial solution pH 2 and pH 7, are shown in Fig. 4 and Fig. 5, respectively. The pH_{pzc} value of both

Table 2. Indexes of dye solutions treated using activated carbon Norit RB 08.CC and Macronet MN 200

Dye solution before treatment			Dye solution treated using AC Norit RB 08.CC			Dye solution treated using Macronet MN 200		
Cr, mg/l	COD, mgO ₂ /l	pH	pH	Cr, mg/l	COD, mgO ₂ /l	pH	Cr, mg/l	COD, mgO ₂ /l
0.62	73.5	2.0	1.8	0	40	1.9	0	10
		7.0	9.7			6.9		
1.23	147	2.0	1.6	0	55	1.9	0	40
		7.0	10.3			6.8		
3.08	367.5	2.0	1.5	0	77	1.9	0	52
		7.0	10.3			6.9		
6.16	735	2.0	1.45	1.50	99	1.9	0	57
		7.0	10.3	3.58	135	6.9	1.25	63
12.32	1102.5	2.0	1.4	4.05	172	1.9	1.81	75
		7.0	10.3	7.90	440	6.9	3.60	84

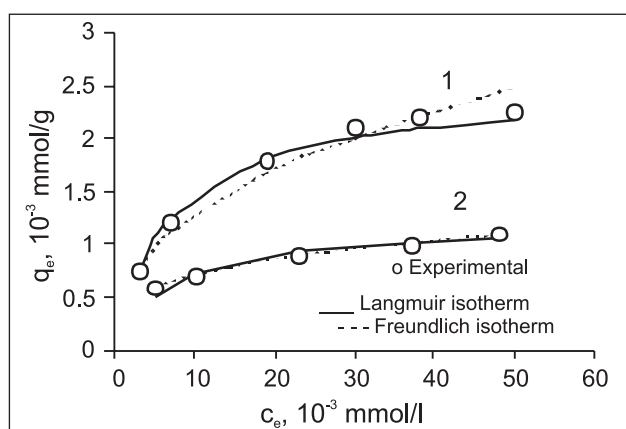


Fig. 4. Adsorption isotherms for dye by activated carbon Norit RB 08.CC at pH 2 (1) and pH 7 (2): experimental data and comparison of isotherm models (conditions: sorbent 0.5 g; 25 ml dye solution, contact time 24 h; temperature 293 K)

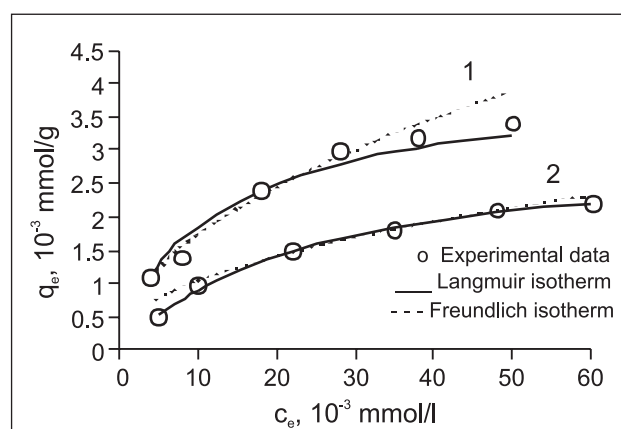


Fig. 5. Adsorption isotherms for dye by Macronet MN 200 adsorbent at pH 2 (1) and pH 7 (2): experimental data and comparison of isotherm models (conditions: sorbent 0.5 g; 25 ml dye solution, contact time 24 h; temperature 293 K)

sorbents (activated carbon and MN 200) are higher than the experimental pH 2, indicating the occurrence of a positive charge in the whole net of both sorbents in the acidic solution which is favourable for dye anion adsorption, whereas during dye adsorption on activated carbon from a neutral solution, the pH value increases from 7 to about 10 (Table 2), and the surface of activated carbon becomes increasingly negatively charged; consequently, the electrostatic repulsive interactions become more important.

The shape of the isotherms indicates L2-behaviour according to the Giles and Smith classification [34]. In L2-type isotherms, adsorption of solute on the adsorbent proceeds until a monolayer is established, the formation of more than one layer being impossible. The study adsorbents effectively remove the dye at low initial concentrations; at higher concentrations, the isotherms reach a maximum capacity as indicated by a plateau of the data. Most of the reported adsorption isotherms of ionic and reactive dyes were L2-type [16, 18, 35]. L2-type isotherms are usually associated with ionic solute adsorption (e. g., metal cations and ionic dyes) with a weak competition with the solvent molecules [34]. Accordingly, an anionic dye favourably adsorbs on the surface with a low competition from water molecules, this adsorption process continuing until the surface concentration reaches the maximum value. In addition, the formation of multi-layers of the adsorbate was not possible due to the electrostatic repulsion between adsorbed ions and those present in the solution. The correlation of the experimental data with the Langmuir and Freundlich adsorption models was checked to gain an understanding of the adsorption behaviour and the heterogeneity of the sorbent surface. The Langmuir model equation is applicable to a homogeneous adsorption system when there is no interaction between the sorbate molecules, while the Freundlich model empirical equation is used to describe heterogeneous systems and is not restricted to the formation of the monolayer.

The Langmuir equation can be represented as follows [36]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}, \quad (5)$$

where C_e (mmol/l) is the equilibrium concentration of the dye in solution, q_e (mmol/g) is the surface concentration of the dye at equilibrium, q_m (mmol/g) is the amount of dye adsorbed at a complete monolayer coverage, and K_L (l/mmol) is the affinity parameter.

The Freundlich model can take the following form [37]:

$$q_e = K_F C_e^{1/n}, \quad (6)$$

where K_F (mmol/g (l/mmol)^{1/n}) represents the adsorption capacity when the dye equilibrium concentration (C_e) equals 1; $1/n$ represents the degree of the dependence of adsorption on equilibrium concentration.

The model equations can be linearized, leading to

$$\frac{1}{q_e} = \left(\frac{1}{q_m K_L} \right) \times \frac{1}{C_e} + \frac{1}{q_m} \quad (7)$$

and

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (8)$$

and fitted to experimental data. The values of K_L and q_m are evaluated from the slope and intercept of the plot of $1/q_e$ vs $1/C_e$ (Eq. 7). The values of $1/n$ and K_F are evaluated from the slope and intercept of the plot of $\ln q_e$ vs $\ln C_e$ (Eq. 8). The corresponding parameters (as obtained from linear-regression analysis) and correlation coefficients (R^2) are presented in Tables 3 and 4.

Table 3. Parameters of the Langmuir model

Sorbent	pH	K_L (l/μmol)	q_m (μmol/g)	R^2
AC Norit RB 08.CC	2–1.4	0.143	2.46	0.9789
	7–10.3	0.138	1.21	0.9933
Macronet MN 200	~2	0.093	3.88	0.9626
	~7	0.040	3.13	0.9976

Table 4. Parameters of the Freundlich model

Sorbent	pH	K_F (μmol/g(l/μmol) ^{1/n})	$1/n$	R^2
AC Norit RB 08.CC	2–1.4	0.49	0.41	0.9777
	7–10.3	0.39	0.27	0.9947
Macronet MN 200	~2	0.53	0.51	0.9848
	~7	0.37	0.45	0.9926

The correlation of chromium complex dye adsorption data with the Langmuir (Table 3) and Freundlich (Table 4) isotherm models was high, the R^2 values being 0.9626–0.9976. As shown in Table 3, the maximum adsorption values for the dye q_m obtained from a correlation of the adsorption data with the Langmuir isotherm model depend on solution pH for the sorption on both activated carbon and Macronet MN 200: the q_m values obtained at solution pH ≤ 2 are higher as compared with q_m obtained at solution pH ≥ 7. K_L represents the equilibrium adsorption constant, therefore, higher values of K_L were indicative of a favorable adsorption process. A comparison of the K_L values shows that both solution pH values studied (pH 2 and pH 7) were favorable for the adsorption of dye on activated carbon (at pH 2 K_L = 0.143, at pH 7 K_L = 0.138 l/μmol), whereas, solution pH 2 is twice as favorable as pH 7 for dye adsorption on Macronet MN 200 (at pH 2 K_L = 0.093, at pH 7 K_L = 0.040 l/μmol).

The Freundlich isotherm satisfactorily describes adsorption on both sorbents exclusively at low concentrations of

solutions (before 30 $\mu\text{mol/l}$) and pH 2 (Fig. 5). The degree of adsorption for the chromium complex dye on MN 200 was higher than on activated carbon, as inferred from the values of K_p , from 0.37 to 0.53 $\mu\text{mol/g}$ and from 0.39 to 0.49 $\mu\text{mol/g}$, respectively (Table 4). The values for $1/n$ were less than unity, which reflects a favorable adsorption on activated carbon as well as on MN 200. The $1/n$ slope is a measure of adsorption intensity or surface heterogeneity, being more heterogeneous for activated carbon than for MN 200 as its value gets closer to zero.

The higher dye adsorption capacity on MN 200 than on activated carbon can be also illustrated by the q_m values of the Langmuir model (i. e. q_m for MN 200 was 3.13 to 3.88 $\mu\text{mol/g}$ and q_m for activated carbon was 1.21 to 2.46 $\mu\text{mol/g}$ (Table 3).

A direct comparison of data obtained in this work with those reported in the literature is not possible since different activated carbons and polymeric adsorbents were used, the dyes and the experimental conditions being not the same, either.

Thermodynamic parameters

In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. Gibb's free energy change, ΔG^0 , is the fundamental criterion of spontaneity. Reactions occur spontaneously at a certain temperature if ΔG^0 is a negative value. The thermodynamic parameters of Gibb's free energy change, μG^0 , enthalpy change, μH^0 , and entropy change, μS^0 , for the adsorption processes are calculated using the following equations [38]:

$$K_c = \frac{C_0 - C_e}{C_e}, \quad (9)$$

$$\Delta G^0 = -RT \ln K_c, \quad (10)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}, \quad (11)$$

where K_c is the equilibrium constant, and C_0 and C_e are the initial and equilibrium solution concentrations, mmol/l, respectively; R is the gas constant (8.314 J/mol K). ΔH^0 and ΔS^0 were obtained from the linear Van't Hoff plot of $\ln K_c$ versus $1/T$ and presented in Tables 5 and 6 for activated carbon and Macronet MN 200, respectively. The thermodynamic equilibrium constant can be replaced with the K_c equilibrium constant, as the concentration of the dye in the solution is relatively low, so that the activity coefficients of the adsorbed dye and the dye in solution approach unity.

The negative values of ΔG^0 confirm the feasibility of the process and the spontaneous nature of adsorption with a high preference of dye by both sorbents under study. The negative values of standard enthalpy change (ΔH^0), obtained for dye adsorption onto activated carbon, indicate the exothermic

nature of the process, while the positive ΔH^0 values obtained for dye adsorption onto Macronet MN 200 indicate the endothermic nature of the process. It is generally accepted that adsorption processes are exothermic due to the heat released after bond formation between the solute and the adsorbent [30]. However, several authors have reported endothermic adsorption of reactive dyes on different types of adsorbents [17, 39]. Entropy ΔS^0 has been defined as the degree of chaos of a system. The positive values of ΔS^0 show an increased disorder at the solid / solution interface during the adsorption of dye onto both activated carbon (Table 5) and the polymeric adsorbent (Table 6). In addition, the values of ΔS^0 are higher at solution pH 2 than that at pH 7.

Table 5. Thermodynamic parameters for dye adsorption on activated carbon Norit RB 0.8 CC (conditions: sorbent 0.5 g, 40 μmol / dye solution 25 ml)

Temperature (K)	q_e ($\mu\text{mol/g}$)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)
pH 2				
293	1.32	-2.437	-3.769	5.09
313	0.99	-1.882		
333	1.11	-2.243		
pH 7				
293	0.32	-0.460	-0.817	1.36
313	0.11	-0.295		
333	0.21	-0.417		

Table 6. Thermodynamic parameters for dye adsorption on Macronet MN 200 (conditions: sorbent 0.5 g, 40 μmol / dye solution 25 ml)

Temperature (K)	q_e ($\mu\text{mol/g}$)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)
pH 2				
293	1.17	-2.127	1.446	12.02
313	1.2	-2.199		
333	1.29	-2.623		
pH 7				
293	0.34	-0.482	0.226	2.49
313	0.40	-0.591		
333	0.37	-0.576		

CONCLUSIONS

The polymeric adsorbent Macronet MN 200 and activated carbon Norit RB 0.8 CC were shown to be effective in removing the anionic dye Lanasyne Navy M-DNL (chromium complex dye) from acidic and neutral solutions.

The degree of dye sorption depends on chromium complex dye concentration, solution pH and temperature. The adsorbents exhibit a higher sorption potential at pH 2 than that at pH 7, presumably because of a positive surface net charge ($\text{pH}_{\text{pzc}} > \text{pH}$). The hypercrosslinked matrix and surface acidity of MN 200 (the total acid 0.2 mmol/g) are more favourable than the surface basicity of activated carbon (the total acid

0.03 mmol/g; the total base 0.5 mmol/g) for the sorption of the chromium complex dye. In identical conditions ($\text{pH} \leq 2$ and temperature 273 K), the polymeric adsorbent Macronet MN 200 removed the chromium complex dye more effectively than did activated carbon: the maximum adsorption values as described using the Langmuir isotherms model on Macronet MN 200 and activated carbon were 3.88 $\mu\text{mol/g}$ and 2.46 $\mu\text{mol/g}$, respectively.

The sorption of the chromium complex dye was found to be spontaneous at the study temperatures (293–333 K) as indicated by the negative values of free energy (ΔG^0). The exothermic nature of sorption is appropriate for chromium complex adsorption on activated carbon (the negative values of standard enthalpy change, ΔH^0), while on Macronet MN 200 the endothermic nature of adsorption is suitable (the positive ΔH^0 values). With an increase in the solution temperature from 297 K to 333 K, the sorption capacity for AC decreases and for MN 200 increases.

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CHROMO KOMPLEKSINIO DAŽIKLIO SORBCIJA AKTYVINTOSIOMIS ANGLIMIS IR NEUTRALIU POLIMERINIU ADSORBENTU

Santrauka

Darbe buvo tiriamas chromo kompleksinio dažiklio sorbcijos bazi-
nėmis aktyvintosiomis anglimis Norit RB 08.CC (AA) ir neutraliu
polimeriniu sorbentu Macronet MN 200 (MN 200) priklausomu-
mas nuo dažiklio tirpalo koncentracijos, pH ir temperatūros bei
sorbento paviršiaus funkcinių grupių prigimties ir elektrinio krūvio
ženklų. Sorbentų sorbcinė geba priklauso nuo tirpalo pH, kuriam
mažėjant – didėja. Sorbuojant dažiklį iš rūgščių ir neutralių tirpalų

polimerinio adsorbento MN 200 sorbcinė geba yra didesnė nei ak-
tyvintųjų anglių. Langmiuro ir Froindlichio izotermų modeliai tinka
eksperimentiniams duomenims analizuoti. Didžiausia Langmiuro
adsorbcijos geba, nustatyta 4–80 $\mu\text{mol/l}$ dažiklio tirpaluose, esant
pH 2 ir 293 K temperatūrai, lygi 2,46 $\mu\text{mol/g}$ AA ir 3,88 $\mu\text{mol/g}$
MN 200. Didėjant dažiklio tirpalo temperatūrai nuo 293 iki 333 K,
dažiklio sorbcija AA mažėja, o MN 200 – didėja. Abu sorbentai efek-
tyviai pašalina chromo jonus ir organinius junginius iš modelinių
tirpalų (pH 2, Cr < 6,16 mg/l, ChDS < 735 mgO_2/l): liekamoji chro-
mo koncentracija tirpale yra mažesnė nei 1,5 mg/l; tirpalo ChDS
mažesnis nei 100 mgO_2/l .

Polimerinis adsorbentas MN 200, kaip ir aktyvintosios anglys,
gali būti naudojamas chromo kompleksiniam dažikliui pašalinti iš
vandeninių tirpalų.