SORPTION OF CATIONIC DYES
ONTO BARKS AND LEAVES OF EUROPEAN TREES

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ABSTRACT

Sorption of Methylene Blue (MB) and Malachite Green (MG) dyes onto barks and leaves of four trees was examined with a batch method. The obtained sorption isotherms are well described by the Langmuir equation. The examined barks proved to have quite different sorption capacities. The highest values were recorded for the walnut tree bark (512 and 307 mg/g towards the MB and MG dyes, respectively) and the lowest capacities were observed for the birch tree bark (68 and 22 mg/g towards the MB and MG dyes, respectively). The studied leaves proved to have rather similar sorption capacities, i.e., from 210 to 286 mg/g for the MB dye and from 152 to 189 mg/g for the MG dye. The specific surface values calculated from the MB monolayer capacity are substantially higher than those obtained by the BET method, probably because of swelling of the test materials in an aqueous medium.

Keywords: low-cost sorbent; Langmuir model; specific surface area, swelling

INTRODUCTION

In the recent decade numerous investigations have been performed on the sorption properties of low-cost materials with the aim of remediation of industrial waste waters [1-5]. Quite good sorbents have been found among clay minerals and agricultural wastes [1,4]. Another group of alternative sorbents appears to be forestry wastes, especially sawdust, bark and leaves. The quantity of such residues in Poland has been estimated at the level of 8 mln m^3 per annum (approximately 26% of total raw wood material). Wood residues come mainly from saw-mills and pulp-mills as well as from the production of wood-based panels [6].

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Literature reports on the sorption ability of barks and other wood wastes concern mainly the sorption of heavy metal ions [7-9]. Meanwhile, literature data on the sorption of aromatic contaminants on wooden byproducts are rather scarce. For example, aspen wood cuttings were used for removal of dissolved polycyclic aromatic hydrocarbons from the aqueous phase [10]. It was found that the effectiveness of the process was satisfactory and not affected by changes in water temperature or pH. Another kind of wood waste, i.e., bark, has also shown affinity to dyes. Sorption of reactive dyes on eucalyptus bark has been thoroughly studied through factorial experiments [11,12]. Eucalyptus bark has been shown to be a very efficient sorbent for anionic dyes as well [13]. Sorption of the Safranine and Methylene Blue cationic dyes onto teak wood bark has been studied in both batch and column modes [1]. The sorption ability of pine bark has been examined with the help of the Methylene Blue dye [14]. A number of studies have also been performed on the sorption properties of tree leaves, the MB dye being used as a probe [15-18]. The leaves examined, coming mainly from subtropical trees, have been reported to have very good sorption properties. For example, the uptake of the MB dye by the guava leaf powder has been reported to be as high as 295 mg/g [15]. Systematic studies on the sorption properties of leaves of the Neem tree widespread in the Indian sub-continent have been performed, too [16,19-21]. The Langmuir sorption capacity of the Neem leaf powder has been determined to be 500, 215, 41 and 20 mg/g for the Rhodamine B, Brilliant Green, Congo Red and Methylene Blue dyes, respectively. Sorption of dyes on bark and leaf materials is assumed to occur due to interactions between the hydroxyl and amino groups of the dyes and hydroxyl, amino and ester moieties of the waste cellulosic material [13,21].

In the present study the barks and leaves of four kinds of trees widespread in Europe have been examined as possible sorbents for cationic dyes.

EXPERIMENTAL METHODS
Preparation and characterization of sorbents

The barks and leaves of birch (Bi), maple (Ma), walnut (Wa) and willow (Wi) trees were collected in Northwestern Poland in the autumn of 2008. The raw materials were washed twice with distilled water, dried at 353 K, milled and sieved (100 mesh). Their BET surface areas, S_{BET}, were determined by means of a GEMINI 2360 surface analyzer. The wide-angle X-ray diffraction patterns of the samples were obtained in a reflection mode using a SEIFERT diffractometer working on CuKα line. Microphotographs of the sorbents were made by means of Nikon Eclipse E400POL microscope. The wet sorbent samples for XRD measurements and microscopy were prepared by swelling in distilled water for 24 hours at ambient temperature.
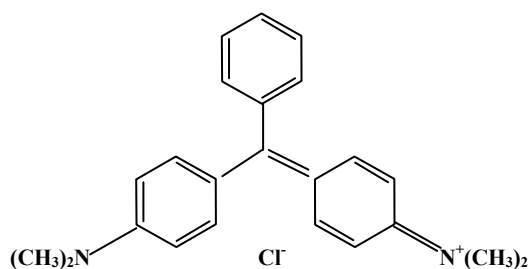
Sorption experiments

Reagent grade Methylene Blue (MB) and Malachite Green (MG) dyes were obtained from POCH (Poland). The structural formulas of the dyes are shown below.

Methylene Blue,
$C_{16}H_{18}N_3SCl$
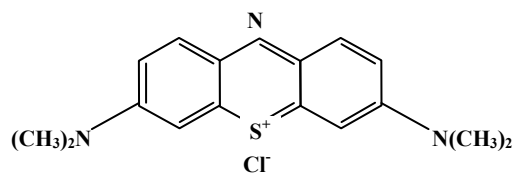
Malachite Green,
$C_{23}H_{25}N_2Cl$

All the sorption experiments were carried out in deionized water in magnetically stirred conical flasks at a room temperature. Kinetic curves were obtained from the experiments with 0.4 dm^3 of the dye solution of 5 mg/dm^3 and 0.1 g of the sorbent. Results of measurements indicate that the time of reaching a sorption equilibrium strongly depends on the kind of sorbent. The lowest values were observed in the systems comprising a dye solution and bark (min. time equal to 90 min. for Wa bark) whereas the highest ones for the systems comprising a dye solution and leaf powder (max. time equal to 4.5 hours for Bi leaves). Typical kinetic plots are shown in Fig. 1. The sorption isotherms were determined in the experiments with 0.1 dm^3 of the dye solutions of a certain concentration and 0.1 g of the sorbents at the contact time of 5 hours. The equilibrium dye concentrations were determined by means of a SHIMADZU MultiSpec-1501 spectrophotometer at wavelengths 667 nm (MB) and 619 nm (MG). The sorption values, a (mg/g), were calculated from the concentration difference:

$$a = (C_o - C) \cdot V / m \qquad (1)$$

where:

C_o, C (mg/dm^3) –   are initial and equilibrium dye concentrations,
V (dm^3)   –   denotes the dye solution volume,
m (g)   –   stands for the sorbent mass.

The obtained sorption isotherms were described by the Langmuir equation:

$$a = a_m \cdot (k_L \cdot C) / (1 + k_L \cdot C) \qquad (2)$$

where:

  a_m (mg/g) – denotes the sorption capacity of the test material,
  k_L (dm^3/mg) – is the Langmuir constant.

The values of specific surface of the sorbents, S_{MB} (m^2/g), were also calculated from the Methylene Blue dye sorption data according to the equation:

$$S_{MB} = a_m \cdot N_A \cdot \omega / M_{MB} \cdot 1000 \qquad (3)$$

where:

  N_A – is the Avogadro constant,
  ω – denotes the surface area occupied by a single MB molecule,
  M_{MB} – stands for MB molecular weight (M_{MB}= 320 g/mol).

The ω value was estimated to be $135 \cdot 10^{-20}$ m^2/molecule [22]. The efficiency of the dye removal was calculated as follows:

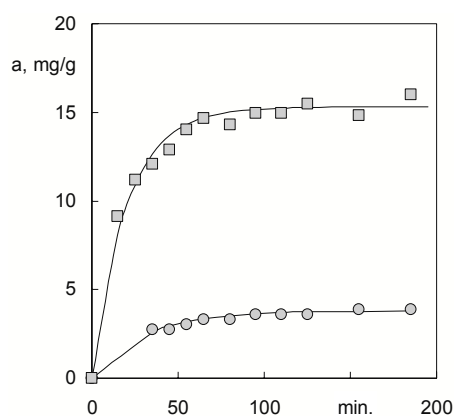$$W = (C_o - C) / C_o \cdot 100\% \qquad (4)$$

Fig. 1. Kinetic curves of sorption of the MB (○) and MG (Δ) dyes on the walnut tree bark.

RESULTS AND DISCUSSION
Sorption isotherms and capacity values

  The obtained isotherms of the cationic dye sorption onto the tree barks and leaves are presented in Fig. 2. The experimental data have been described by the Langmuir equation. The obtained values of monolayer sorption capacity and Langmuir constant are shown in Table 1.
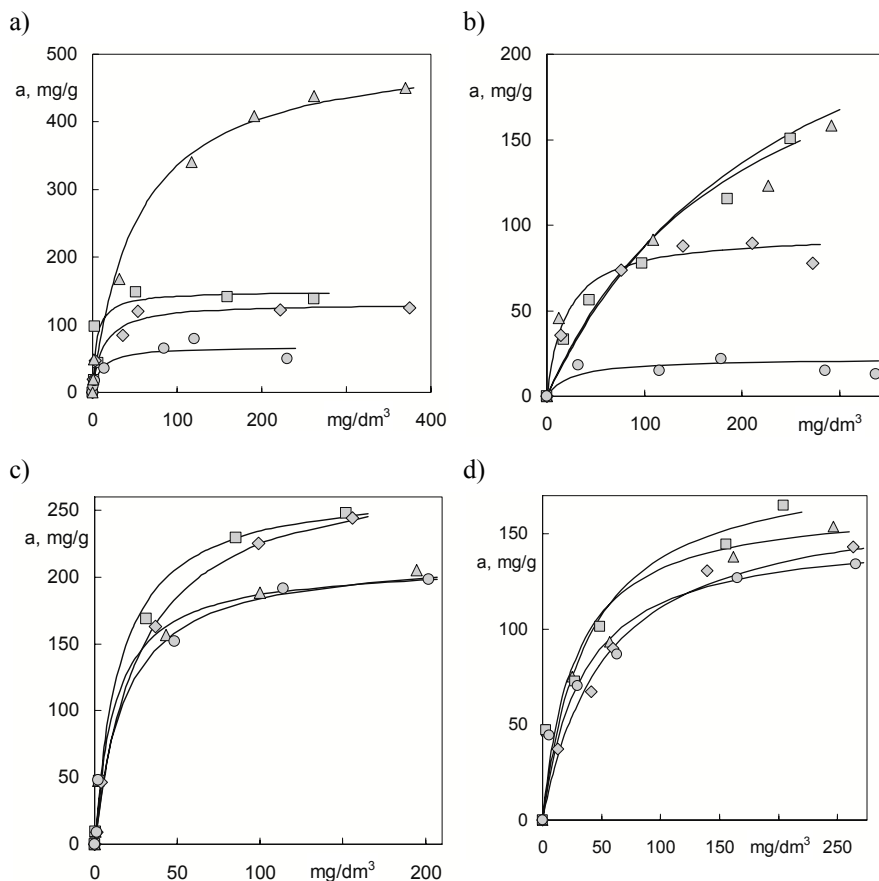
a)

b)

c)

d)

Fig. 2. Sorption isotherms of the MB (a,c) and MG (b,d) dyes on the birch (○),
maple (◊) walnut (Δ) and willow (□) tree barks (a,b) and leaves (c,d). The
lines correspond to the Langmuir plots at the parameters listed in Table 1.

The sorption capacity values resulting from the Langmuir equation for
the studied barks proved to be somewhat scattered. The highest sorption
capacity values, 512 mg/g and 307 mg/g for the MB and MG dyes,
respectively (see Table 1), have been obtained for the walnut tree bark. The
lowest sorption capacity has been recorded for the birch tree bark – 68 mg/g
for the MB dye and 22 mg/g for the MG dye. The obtained values of
sorption capacity of the studied barks towards the Methylene Blue dye
proved to be rather similar to those reported in other works. For example,
sorption of the MB dye on the Soxhlet extracted pine bark is equal to
115 mg/g [14]. Sorption of the Methylene Blue dye on teak wood bark has
been determined to be as high as 914 mg/g [1].

In contrast to the barks, leaf sorbents proved to have rather similar sorption capacities, ranging from 210 to 286 mg/g for the MB dye and from 152 to 189 mg/g for the MG dye (Table 1). The most similar literature data on the sorption capacity of leaves towards the Methylene Blue dye equal to 295 and 133 mg/g have been reported for guava leaf powder [15,17]. The sorption capacities of the Neem tree leaves and phoenix tree leaves toward the MB dye have markedly lower values, i.e., 19.6 mg/g [16] and 81 mg/g [18], respectively.

Apparently, the observed differences in sorption values result from both the sorbent composition and the molecular structure of the dye. Wood materials are composed of cellulose, hemicelluloses, lignin and others. It was shown that lignin is remarkably responsible for the sorption abilities of such composites [23]. As a hydrophobic polymer wood lignin sorbs hydrophobic organic matter (and aromatic hydrocarbons among them) from aqueous solutions [24]. Comparing the values of sorption capacities observed for the examined sorbents towards a certain dye (Table 1) one can assume that bark materials are richer in the lignin component, compared with leaves.

The structure of sorbate molecules is a second factor limiting the sorption value. Boving et al. observed [10] that aspen wood cuttings adsorb high molecular weight polycyclic aromatic hydrocarbons more effectively than do low molecular weight ones. In the present study compounds of comparable molecular weight (i.e., 320 and 365 g/mol for MB and MG, respectively) were sorbed but values a_m obtained for MB appeared markedly higher than those for MG. Probably molecules having a linear molecular structure (MB) are better adjusted to the sorbent surface than those with a branched structure (MG), which are hindered to be tightly packed. A similar regularity was observed for adsorption of the cationic dyes on kaolin surface as well [25].

The Langmuir constant values, K_L, describe the attraction strength between the sorbate molecules and sorbent surface. In general, one can infer that bonds of the cationic dyes with the analyzed materials are durable (Table 1). However, a certain correlation between the K_L value and the dye structure has been noticed. In the systems containing the MB dye (linear molecules) bonds were strong, especially when the Wi bark or the Bi bark were used as sorbents. On the contrary, MG molecules (branched structure) were bonded visibly weaker. The shapes of the respective sorption curves (Fig. 2) confirm the above-mentioned observations.

Table 1. A numerical characteristics of the sorbents studied.

sorbent		specific surface area		Langmuir equation parameters				dye removal extent*, % at initial dye concentration			
				MB dye		MG dye		MB dye		MG dye	
		S_{BET}, m²/g	S_{MB}, m²/g	a_m, mg/g	k_L, dm³/mg	a_m, mg/g	k_L, dm³/mg	50 mg/dm³	200 mg/dm³	50 mg/dm³	200 mg/dm³
barks	Ma	12	335	132	0.08	95	0.05	93	73	71	22
	Wa	25	1300	512	0.019	307	0.004	97	84	91	46
	Wi	42	378	149	0.2	264	0.005	88	15	66	9
	Bi	54	173	68	0.1	22	0.04	72	6	36	11
leaves	Ma	28	726	286	0.037	170	0.019	92	82	75	19
	Wa	16	533	210	0.08	167	0.037	95	78	94	25
	Wi	14	685	270	0.065	189	0.026	95	84	94	36
	Bi	6	551	217	0.055	152	0.03	96	76	89	27

*at a sorbent load of 1 g/dm³

Specific surface and structure of the sorbents

Data in Table 1 clearly indicate that sorption capacities do not correlate with the specific surface values obtained by means of the BET method. For instance, among the barks studied, the one of the birch tree which has the highest specific surface value proved to have the lowest sorption capacity (Table 1). One more observation is that specific surface values measured by the BET method are substantially lower than those estimated from the MB dye sorption. This difference was observed for all the materials studied (Table 1). Apparently, the observed discrepancy resulted from different conditions during the specific surface measurements – the BET method data characterize dry materials whereas the MB sorption data characterize wet ones. It is obvious that all the examined materials are cellulose-based ones and, therefore, they are able to swell in aqueous media. That is why, the accessible surface of the wet materials increases, resulting in the sorption capacity increase. The leaves and bark swelling is directly confirmed by the microphotographs (Fig. 3) indicating clearly that the mean dimensions of the wet material particles are larger than those of the dry ones.
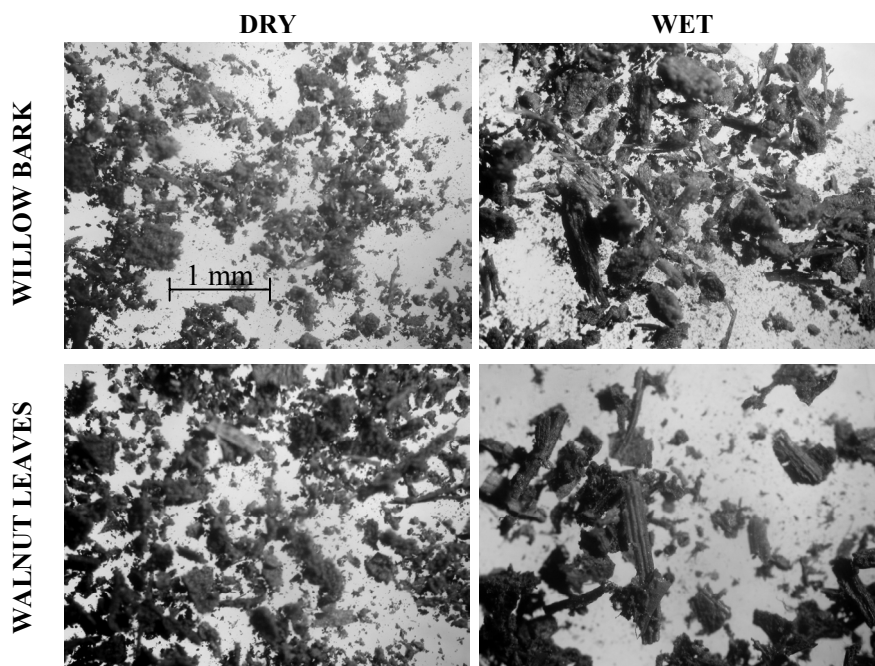

Fig. 3. Microphotographs of sorbents shown in the examples under dry and wet conditions.

Some additional data on the bark structure and swelling have been obtained by comparing the X-ray diffraction patterns of the dry and wet materials (Fig. 4). The diffractogram of the dry maple bark revealed two weak peaks at 2 theta angle values ca. 15° and 22° ascribed to cellulose [26]. The diffractograms of the dry walnut and willow barks contain only a very weak peak at 15°. The diffractogram of the birch bark does not contain any peaks, which indicates that the birch bark is practically amorphous. The order of molecular arrangement decrease (Ma > Wa $\cong$ Wi > Bi) is in full agreement with the BET surface data: the lesser is the bark structure ordering the larger is the dry bark surface value (see for the S_{BET} values in Table 1). Under wet conditions, the diffraction peaks decrease (maple bark) or disappear (walnut and willow barks), indicating that the structure ordering of the barks decreases substantially – see Fig. 4. The registered structure disordering agrees well with the high surface values estimated for the wet barks (see for the S_{MB} values in Table 1). On the other hand, diffractograms of all the leaves studied (not shown) contain no peaks that indicate that no molecular arrangement takes place under either dry or wet conditions. The registered amorphous state agrees well with the high specific surface values observed for all the leaves studied (Table 1).
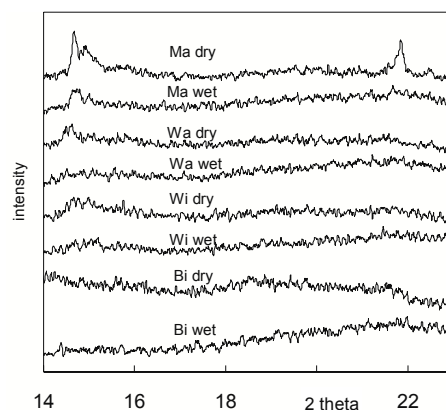

Fig. 4. X-ray diffractograms of the barks studied under dry and wet conditions.

Decolourization efficiency

The efficiencies of decolourization of the dye solutions are high enough suggesting the studied materials could be used in practice. Both the barks and leaves applied at the load of 1 g/dm^3 towards the MB solutions of initial concentration of 50 mg/dm^3 resulted in very efficient decolourization (Table 1). Decolourization of the MG dye solution looks somewhat less efficient (Table 1). The extent of dye removal is naturally decreased with the increase in dye concentrations (Table 1).

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CONCLUSIONS

The barks and leaves of birch, maple, walnut, and willow trees in the raw form may readily adsorb cationic dyes. All of the examined wood materials proved to have quite high sorption capacities and provide efficient dye removal from aqueous solutions at relatively low sorbent loads. The sorption abilities of the wooden byproducts depend on the structure of the dye molecule. The highest efficiencies of decolourization were observed for the Methylene Blue dye having a linear molecular structure.

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