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Toxic Heavy Metal Ions and Metal-Complex Dyes Removal from Aqueous Solutions Using an Ion Exchanger and Titanium Dioxide

DOI: 10.5604/01.3001.0010.5748

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Abstract

The aim of the study was to compare the removal efficiency of toxic heavy metal ions: chromium(VI), nickel(II) and copper(II) as well as metal-complex dyes from aqueous solution using Lewatite VPOC 1065 and Adsorbisia™ As500. The point of zero charge (pH_{PZC}) of both sorbents and the influence of the initial concentration on the sorption process of Ni(II), Cu(II), Cr(VI), C.I. Acid Red 183 (AR183), C.I. Reactive Blue 21 (RB21) and nickel(II) phthalocyanine-tetrasulfonic acid tetrasodium salt (NiPc-TSATSS) were studied to determine the maximum sorption capacity. Kinetic studies were also carried out for the most effective sorbent-sorbate systems. The concentration effect of both hydrochloric acid and auxiliaries on the removal yield was also taken into account. As was found, Lewatit VPOC 1065 can be successfully applied for the treatment of textile wastewaters containing metal complex dyes and heavy metal ions. The highest sorption capacity, $q_e = 816.1$ mg/g, was found for C.I. Acid Red 183.

Key words: dyes, heavy metals, removal, ion exchangers, titanium dioxide.

Introduction

At present, one of the main problems in the world is the increasing amount of contaminants discharged into the environment as a result of the intensive development of industry, exploitation of its goods and active human activity [1, 2]. Wastewater includes both “used” water and household wastewater, as well as water used in industry. Particular attention should be paid to those branches of industry that consume significant amounts of water in technological processes and thus generate significant quantities of wastewaters containing harmful and toxic substances of carcinogenic properties, which can adversely affect aquatic ecosystems, soil and living organisms, including humans [1-3]. One such branch of industry is undoubtedly the textile industry, which consumes large amounts of water (about 200 l for 1 kg of textile) and considerable quantities of chemical compounds during dyeing, printing and finishing processes [3]. Among the current issues in the field of environmental protection related to the textile industry, increasing costs of wastewater treatment and disposal, increased legislation on the quality of effluent discharge, e.g. toxicity and colour, as well as increasing water supply costs should be mentioned first of all. Toxic pollutants are discharged to the environment from various industries, which originate mainly from the dyeing, textile, paper, cosmetics and pharmaceutical industries, as well as from the electroplating, metallurgy, leather tanning, cement preservation, paint, pigment in-

dustries [1-5]. It should also be emphasised that the annual production of dyes exceeds 700,000 tons, of which about 80% are azo dyes, with the textile industry consuming almost three-quarters of this. Due to the high consumption of dyes by the textile industry this branch produces 100 tonnes of dye per year, which is discharged into the environment [5]. During the dyeing process, a significant portion of the dye is not bound to the fibre (the percentage of unstained dye is from 1 to 50%); however, it depends largely on the type of dye used and fibre being coloured. It should be also taken into account the fact that cotton accounts for 52% of the textile market and that reactive dyes are characterised by the lowest fixation (20-50%). Most of the problems are associated with colouring cotton with this group of dyes [6, 7].

As is commonly known, during the manufacturing process of the finished product, the textile industry consumes not only dyes but also heavy metal ions, phenol and its derivatives as well as auxiliary substances such as salts, bases, acids, surfactants, reducers and oxidants, which appear in the wastewaters etc. In order to increase the sorption of direct and reactive dyes (dyes of low fibre affinity), alkali (NaOH or Na_2CO_3) and significant amounts of salt (NaCl, Na_2SO_4) are used, e.g. the dyeing of cellulosic fibres with reactive dyes requires their addition in an amount corresponding to a concentration of 100 g/l to both salts. Alkalis and reducing agents are responsible for converting

dyes into a soluble form. Detergents are applied for effective washing after dyeing and as wetting and dispersing agents, whereas cationic fixatives used to improve resistance stains on wet factors. Formic acid or acetic acid is added to the bath in order to obtain a suitable pH value and salts (sodium and ammonium sulphates) to obtain uniform colouring [8]. On the other hand, heavy metals can occur naturally in the fibre structure or can be re-introduced into a textile product during manufacturing processes. Such metals can come from dyeing and finishing processes due to the use of metal-complex dyes characterised by good dyeing resistance, the use of acid chromium dyes, especially when dyeing wool and polyamides, as well as cationic, reactive or vat ones. They can also come from the chemical treatment of fibres (improvement of resistance to light and wet factors), fabric bleaching processes where metals are used as catalysts for oxidants, etc [6, 7]. Among metal-complex dyes, chromium ones are often used for the dyeing of polyamide and wool. Moreover heavy metal ions such as cobalt, chromium as well as copper or nickel are constituents of dyes used for the dyeing of leather, polyamide and wool, whereas cationic ones containing zinc, chromium, cadmium and arsenic are used for the dyeing of polyacrylic fibres etc. In turn, the presence of phenol and its derivatives in wastewaters comes from the production processes (e.g. resorcinol, hydroquinone, pyrogallol) of various types of dyes [7]. It is worth mentioning that the above

listed chemicals are classified as persistent impurities, non-biodegradable, and in addition they have toxic, mutagenic and cancerogenic properties. Applying even a small amount of dye can result in an undesirable colour of a large volume of water as well as a reduction in sunlight penetration and photosynthesis [5]. The dyeing of textiles leads to environmental hazards due to the pollution of wastewaters with dyes, heavy metals, phenols, salts, acids, alkalis, surfactants, detergents etc., as well as the consumption of significant amounts of water and energy, and the emission of toxic substances into the air during the heat treatment of textiles [1-3, 5]. Hence it is extremely important to remove such pollutants from waters and wastewaters using various physicochemical methods [9], among which, adsorption plays an important role, i.e. the control of their content in wastewater and the development of new methods of their removal have become a necessity. Therefore the aim of this study was to compare the removal efficiency of toxic heavy metal ions, namely chromium(VI), nickel(II), copper(II), and metal-complex dyes containing these metals, from aqueous solutions using the weakly basic ion exchanger (Lewatit VPOC 1065) and an Adsorbisia™ As500 (TiO₂). The pHPZC of both sorbents and influence of the initial concentration on the sorption process of Ni(II), Cu(II), Cr(VI), C.I. Acid Red 183 (AR183), C.I. Reactive Blue 21 (RB21), and nickel (II) phthalocyanine-tetrasulfonic acid tetrasodium salt (NiPc-TSATSS) were determined to estimate the maximum sorption capacity (equilibrium studies). Kinetic studies of the sorption process were also carried out for the most effective sorbent-sorbate system. The effects of hydrochloric acid concentration (for heavy metal ion systems) as well as auxiliaries such as sodium sulfate (VI), acetic acid and SDS (sodium dodecyl sulfate, for the dye containing systems) on the removal yield was also taken into account.

Experimental

Sorbates and sorbents characteristics

Metal(II) and (VI) working solutions of proper concentration in mg/l were prepared from stock solutions (10 000 mg/l in 0.1 M HCl) by dilution with HCl, whereas working solutions were prepared from such salts as CuCl₂·2H₂O, NiCl₂·6H₂O and K₂Cr₂O₇ which were weighed and dissolved with doubly dis-

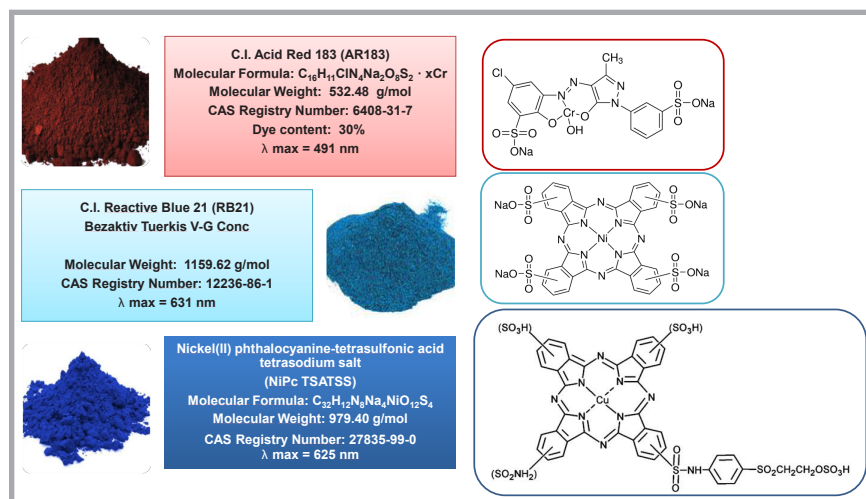


Figure 1. Characteristics of metal complex dyes.

tilled water with HCl addition. Metal-complex dye solutions were prepared by dissolving the exact quantity of dyes with doubly distilled water. The following chemicals: hydrochloric acid, acetic acid, sodium(VI) sulfate, sodium chloride, metal containing salts etc. were purchased from a chemical reagent company – Chempur, Poland, and anionic surfactant sodium dodecyl sulfate dyes (SDS) from Sigma-Aldrich, Germany (used without further purification). The metal-complex dye characteristics applied for sorbate phase preparation are presented in **Figure 1**.

As a sorbent phase, the weak basic anion exchange resin Lewatit VPOC 1065 as well as titanium dioxide Adsorbisia™ As500 were used. Their physicochemical properties are shown in **Table 1** [29, 30].

Point of zero charge determination

The pH of zero point charge (pHZPC) of Lewatit VPOC 1065 as well as Adsorbisia™ As500 were determined using the solid addition method [10]. Solutions of 0.01 M KNO₃ concentration


and proper pH, which was in the range from 1 to 12, were prepared using 0.1 M HCl and 0.1 M NaOH. Then 0.5 g of sorbent was brought into contact with 50 ml of solution for 24 hours (vibration amplitude A = 8 units, shaking speed V_w = 180 spm). After this period of time, the pH of the solution was measured again using a pH-meter CP-411 (Elmetron, Zabrze, Poland).

Batch studies of sorption efficiency

The sorption process was investigated using a mechanical shaker (Elpin+, type 357, Lubawa, Poland) and the static method. Initially the maximum sorption capacities for the sorbates studied for the anion exchange resin Lewatit VPOC 1065 and mineral oxide TiO₂ were determined (isotherm studies) in order to select the most effective sorbate-sorbent systems.

Sorbate sorption tests were done in 100 cm³ conical flasks, sealed with silicone plugs. Sorbent (anion exchange resin Lewatit VPOC 1065 or TiO₂) in the amount of 0.5 g, weighed with the ac-

Table 1. Physicochemical properties of Lewatit VPOC 1065 and Adsorbisia™ As500 [29, 30].

Sorbent	Lewatit VPOC 1065	Adsorbisia™ As500
Functional group	primary amine, benzylamine	
Matrix	crosslinked polystyrene	
Structure	macroporous	
Bead sizes	0.315 – 1.25 mm	0.25 – 1.19 mm
Effective size	0.47 – 0.57 mm	
Total capacity	2.2 eq/L	Arsen(V) 12 – 15 g/kg Arsen(III) 3 – 4 g/kg Selen(IV) 4 – 5 g/kg
BET Surface area	~ 50 m ² /g	200 m ² /g
Pore volume	0.27 cm ³ /g	0.4 cm ³ /g
Pore diameter	25 nm	–

curacy ± 0.0005 g, was placed in the flask, and next 50 cm^3 of the initial aqueous solution from 1000 to 100 000 mg/l was added. Thus prepared, the flasks were placed in a mechanical shaker working with the following parameters: $A = 8$ units, $V_w = 180$ spm, room temperature, phase contact time $t = 24$ h. After one day the phase were separated by filtration and the aqueous phase was analysed for the content of metal-complex dyes or heavy metal ions using Ultraviolet-visible spectroscopy (UV-Vis) (Carry 60, USA) or Atomic absorption spectroscopy (AAS) (Varian AA240FS, Australia), respectively. The metal-complex dye concentration after the sorption process was measured in a 1 cm quartz cell at the maximum absorbance wavelength (491 nm – AR 183, 631 nm – RB 21, 625 nm – NiPc TSATSS), with a split width of 1 mm and for an integration time of 1 s. Using a Fast Sequential Atomic Absorption Spectrometer with SIPS autosampler, the concentration of heavy metal ions was obtained at a wavelength of 232.0 nm, 324.8 nm and 357.9 nm; the

lamp current was 4 mA, 4 mA & 6 mA, the slit width – 0.2 nm, 0.5 nm & 0.2 nm and the air/acetylene flow was 13.5/2 l/min for Ni(II), Cu(II) and Cr(III), respectively.

On the basis of the data obtained, the sorption capacities (q_e) were determined using *Equation 1* [9]:

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

where C_0 and C_e in mg/l are the initial and equilibrium concentrations of heavy metal ions or metal-complex dyes, V in l – the volume of solution (0.05 l), and m in g – the mass of Lewatit VPOC 1065 or TiO_2 (0.5 ± 0.0005 g).

Due to the fact that not only the removal efficiency but also the rate of pollution removal from the environment/system is of great importance (a time-consuming process, and thus its economy), for the best systems for which the most satisfactory results were obtained from the isotherm studies, kinetic studies were additionally carried out. The effects

of the phase contact time as well as of the initial heavy metal ions and metal-complex dyes on the sorption process of the sorbate under discussion were analysed using a similar procedure to that described in the isotherm studies. The experimental conditions were as follows: vibration amplitude $A = 8$ units, shaking speed $V_w = 180$ spm, room temperature, phase contact time – from 1 min to 4 h, $t = 1$ min – 4 h, the initial heavy metal concentration – 10, 20 and 30 mg/l, and the initial metal-complex dye concentrations – 100, 500 and 1000 mg/l (the difference in the initial concentration of heavy metal ions and metal-complex dyes was caused by the highly variable efficiency of the sorption process; the capacity values obtained in the equilibrium studies were significantly different, much higher for the metal-complex dyes).

In the next step an attempt was made to examine the effect of hydrochloric acid concentrations (0.1; 1; 3; 6 M HCl) on the effectiveness of the sorption process in the case of heavy metal ions, while in the case of the dye system (AR 183) – Lewatit VPOC 1065, the influence of sodium chloride (0 – 50 g/l), sodium(VI) sulfate (0 – 50 g/l), acetic acid (0 – 2.5 g/l) and anionic surfactant SDS (sodium dodecyl sulphate) (0 – 0.5 g/l) was tested. The initial heavy metal concentration was equal to 20 mg/l (phase contact time – 4 h), whereas that of the initial metal-complex dye was 500 mg/l (phase contact time – 15 min) (the parameters were selected in such a way that the removal % was not equal to 100%, so that the effects studied could be observed, both the increase and decrease in the sorption capacity), with the other parameters being the same as in the kinetic studies.

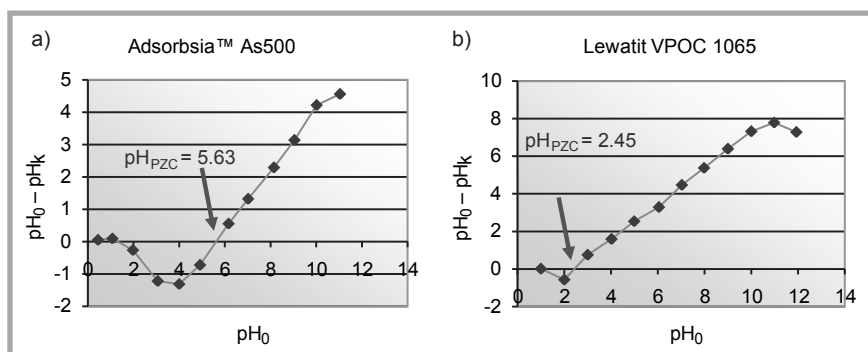


Figure 2. Plot of dependence between $\Delta pH = pH_0 - pH_k$ and pH_0 for a) *Adsorbisia™As500* and b) *Lewatit VPOC 1065*.

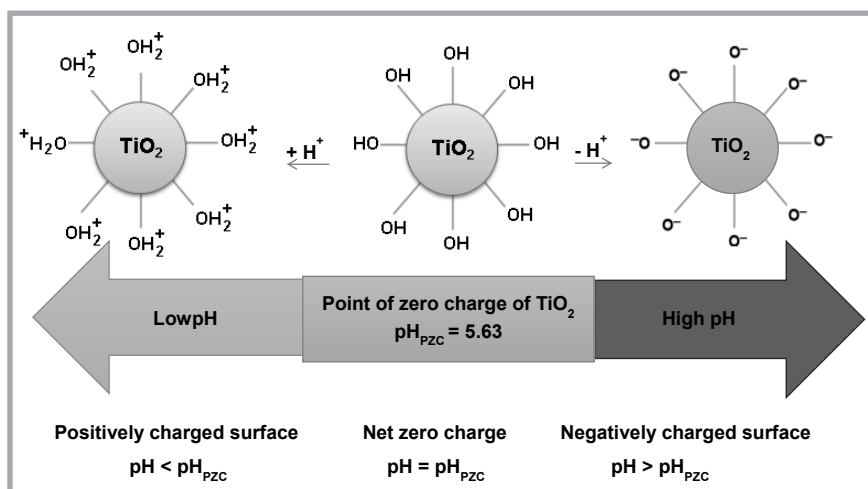


Figure 3. Presentation of the functional groups of TiO_2 in dependence on the pH and pH_{PZC} values.

Results and discussion

Point of zero charge of sorbents under discussion

According to the procedure described in Subchapter **Point of zero charge determination** the pH_{PZC} of both sorbents under discussion was determined. A plot of pH_0 versus the difference between the initial pH of the solution before sorption (pH_0) and the final pH of the solution after sorption (pH_k) was obtained ($\Delta pH = pH_0 - pH_k$) and is presented in *Figure 2*.

As shown in *Figure 2*, the pH_{PZC} of both sorbents was obtained taking into account the intersection point of the curve

with the x axis mentioned. As was found, the pH_{PZC} was equal to 5.63 for Adsorbisia™ As500 and 2.45 for Lewatit VPOC 1065. TiO_2 points of zero charge reported in the literature are usually in the range from 2 to 8.9, whereas the average ones are in the range 5.6 – 5.8 (anatase 5.9 – 6, rutile 5.4 – 5.5) [11]. Depending on the pH_{PZC} , the surface of titanium oxide could be positively or negatively charged, whereas at $pH = pH_{PZC}$ the surface did not possess any charges (**Figure 3**). The functional groups of TiO_2 in dependence on pH_{PZC} can be found in **Figure 3** [12]. In the case of the weak basic anion exchanger, the pH of the solution also plays a significant role in its functionality (**Figure 4**). WBA (weakly basic anion exchange) resins can be usually used in a pH range from 0 to 9. Depending on the solution pH, the functional groups of WBA resins (primary, secondary or tertiary amine) present in a protonated or deprotonated form. Due to the Lewis-base properties of amino groups, they can be bound coordinately with Lewis acids [13, 14].

Equilibrium studies

The effect of the initial concentration of heavy metal ions and metal-complex dyes on the sorption process on Lewatit VPOC 1065 and Adsorbisia™ As500 was investigated to determine the maximum sorption capacities, the results of which are presented in **Figure 5**. On the basis of the results obtained, the following affinity series were determined: Adsorbisia™ As500: RB21 (59.2 mg/g) > AR183 (44.6 mg/g) > Ni(II) (42.8 mg/g) > NiPc – TSATSS (15.67 mg/g) > Cr(VI) (7.44 mg/g) >> Cu(II) (-); Lewatit VPOC1065: AR183 (816.1 mg/g) > Cr(VI) (67.25 mg/g) > RB21 (59.2 mg/g) > Ni (II) (44.88 mg/g) > NiPc – TSATSS (8.8 mg/g) >> Cu (II) (-); (-) – indicates that the sorption was not observed, and the best sorbate (metal-complex dye) – sorbent and sorbate (heavy metal ions) – sorbent were selected for kinetic studies.

As was found, Lewatit VPOC 1065 is a much more effective sorbent compared to titanium dioxide. The sorption capacity values were much higher or slightly higher for the WBA resin for all sorbates under discussion compared to those obtained for titanium dioxide, while better sorption capacities were obtained only for NiPc – TSATSS on titanium dioxide. The sorption capacity values are strongly

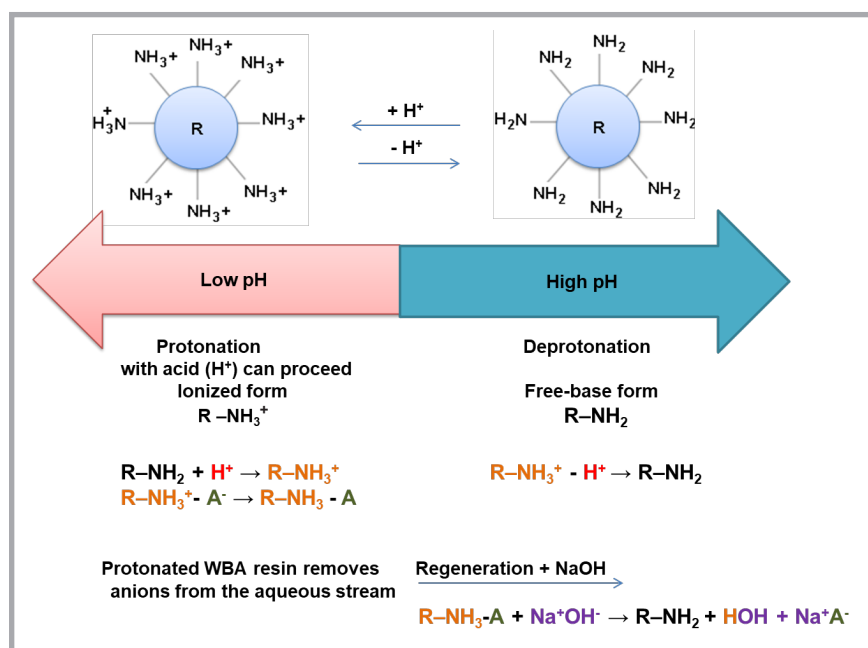


Figure 4. Weak basic anion exchange (WBA) resin functionality in dependence on the pH.

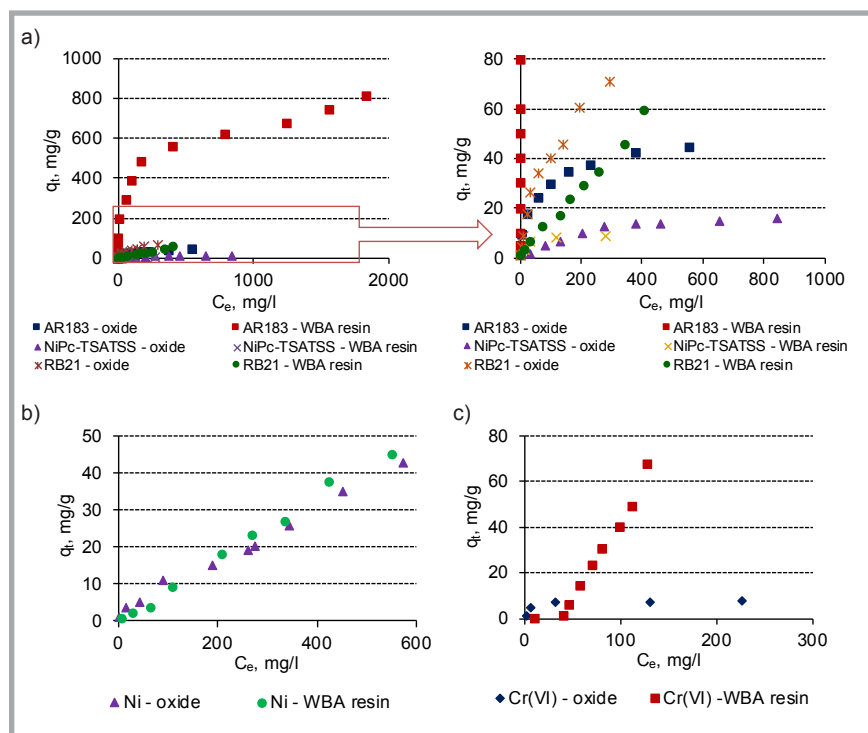


Figure 5. Effect of a) initial metal-complex dyes and b), c) heavy metal ions on sorption on Lewatit VPOC 1065 (WBA resin) and Adsorbisia™ As500 (oxide).

dependent on the sorbate and sorbent properties, among others: the size of the sorbed molecule, the form in which the sorbate exists in the system under discussion, pH of the solutions, the presence of functional groups, their types and content, the surface properties of the sorbate, the BET surface area, pore volume, pore size, porous distribution, sorbent particle type (e.g. powder, beads) etc. [15, 16].

Taking into account the metal sorption on the sorbent, the species in which heavy metal ions exist in the system under discussion play a significant role. All experiments on heavy metal ions were performed in 0.1 M HCl solutions. In such solutions copper(II) exists in the form of anionic complex $CuCl^-$ and Cu^{2+} , nickel(II) in the form of cationic and neutral complexes such as the Ni^{2+} , $NiCl^+$ and $NiCl_2$ [17]. The chromium(VI) species

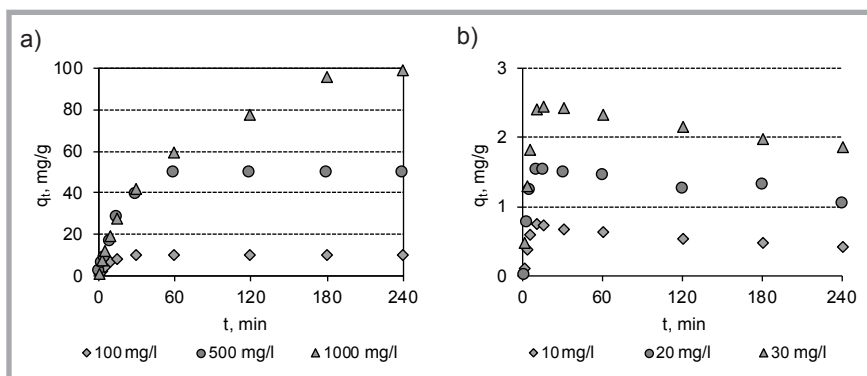
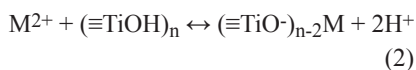


Figure 6. Kinetic curves of a) AR183 and b) Cr(VI) sorption on Lewatit VPOC 1065.

form depends mainly on the pH value and Cr(VI) concentration. In the aqueous solutions the following forms can be found: $\text{Cr}_2\text{O}_7^{2-}$, H_2CrO_4 , HCrO_4^- and CrO_4^{2-} . At acidic pH e.g. pH 2 – 6, HCrO_4^- is predominant, whereas at a neutral and basic pH, pH = 7–10, it is CrO_4^{2-} [18, 19]. The mechanism of heavy metal ion sorption on titanium dioxide is the surface complex formation, inner-sphere surface complexes forming [20] by the interactions of metal ions with the hydroxyl groups of titanium dioxide of amphoteric properties which are produced during the hydrolysis of oxide:



As was shown in **Figure 3**, the protonation and deprotonation of functional groups change the surface charge of titanium dioxide. At low pH, below $\text{pH}_{\text{PZC}} = 5.63$, the surface possesses a positive charge; therefore the chromium(VI) (which exists in an anionic form) sorption is the highest. As was pointed out by Konstantinou and Pashalidis [21], the titanium dioxide particles act as cation exchange resins which bind M^{2+} through the oxygen active sites. Charge neutralisation of M^{2+} by the groups as well as higher affinity for the cation than anion were obtained. Metal-complex dye sorption on titanium dioxide is possible due to hydrogen bonds between the hydroxyl group of titanium dioxide and oxygen atoms in the dye molecule, hydrogen bonds between the hydroxyl group of titanium dioxide and the aromatic ring in the dye, hydrogen bonds between the hydroxyl group of titanium dioxide and the azo group of the dye, and the ion pair between the protonated hydroxyl group and the dissociated sulfonic group of the dye [22].

Sorption on the WBA resin, as mentioned above, for the sorbate under discussion is more effective than on titanium oxide. As was presented in **Figure 4**, in the acidic solutions functional groups of the WBA resin are protonated, therefore they can interact with anionic species e.g. dyes (sulfonic groups of dyes), with the anionic chromium(VI) species resulting in high sorption capacities and ion pair formation. Moreover the higher sorption yield of AR183 on Lewatit VPOC 1065 can be caused by the smallest size of AR183 particles, as compared to the other metal-complex dyes under discussion. Due to the presence of aromatic rings of dyes as well as such rings in the anion exchange resin structure, hydrophobic interactions π - π can also take place. The high affinity of the dyes to the anion exchangers can also result from the formation of hydrogen bonds [23, 24]. Kaušpėdienė *et al.* [24, 25] found that the sorption capacities during phthalocyanine dye (CuPc) sorption on a strongly basic anion exchanger of macroporous structure – Purolite A500PS and hypercrosslinked non-functionalized Macronet MN 200 were 86.9 $\mu\text{mol/g}$ and 2.3 $\mu\text{mol/g}$, respectively, whereas for LanasyN Navy M-DNL (LNCr) and Acid Blue 249 (CuPc) on weakly basic anion exchanger Purolite A847, it was 831.01 mg/kg and 205.22 mg/kg (one-component solutions, column studies), respectively.

Kinetic studies

Based on the equilibrium studies and sorption capacity values, the most effective sorbate-sorbent systems were chosen and applied in kinetic studies to examine the time-dependent behaviour of AR183 and Cr(VI) sorption on Lewatit VPOC 1065. The phase contact time was in the range from 1 min to 4 h, and the amounts of AR183 or Cr(VI) sorbed on the WBA resin as a function of the phase contact

time and initial concentration are depicted in **Figure 6**.

For AR183 the q_t values increase with the increasing phase contact time (e.g. for $C_0 = 100 \text{ mg/l}$ $q_t = 3.8 \text{ mg/g}$ after 5 min of the phase contact time and $q_t = 9.7 \text{ mg/g}$ after 30 min of the phase contact time) as well as with the initial metal-complex dye increase (e.g. for $C_0 = 100 \text{ mg/l}$ $q_t = 9.9 \text{ mg/g}$ after 240 min of the phase contact time; for $C_0 = 500 \text{ mg/l}$ $q_t = 49.6 \text{ mg/g}$ and for $C_0 = 1000 \text{ mg/l}$ $q_t = 98.3 \text{ mg/g}$). Moreover in the first 30 min of the phase contact time, 96.6% ($C_0 = 100 \text{ mg/l}$), 77.9% ($C_0 = 500 \text{ mg/l}$) and 41.7% ($C_0 = 1000 \text{ mg/l}$) of AR183 was sorbed by Lewatit VPOC 1065. The final % of AR183 removal by the WBA resin in all cases was higher than 98.3%. The time required to reach system equilibrium was equal to 120 min ($C_0 = 100 \text{ mg/l}$), and was higher than 240 min ($C_0 = 500$ and 1000 mg/l). As was pointed out by Kaušpėdienė *et al.* [26], the time required to reach equilibrium was 10 – 15 min (pH 2) and 15–30 min (pH 7) for the chromium complex dye LanasyN Navy M-DNL on activated carbon Norit RB 0.8 CC and Macronet MN 200.

At the beginning of Cr(VI) sorption on Lewatit VPOC 1065, a similar trend of q_t value changes to that observed in the case of AR183 was found; but after 30 min of the phase contact time, the q_t values decreased. At 30 min of the phase contact time, the q_t values were equal to 0.7; 1.5; 2.7 mg/g, whereas the % removal was 66.7, 74 & 80.5% for the system of initial concentrations: 10, 20 & 30 mg/l. A decrease in q_t values after 90 min of the phase contact time was previously observed by Wójcik and Hubicki [19] during Cr(VI) sorption on WBA resin Purolite A830. Such behaviour was explained by the fact that the reduction of Cr(VI) to Cr(III) proceeds. Cr(III) concentration in the external solutions increases and the maximum removal efficiency (% $R_{\text{Cr(III)}} + \text{Cr(VI)}$) was 71% at 90 min of the phase contact time [19].

Effect of hydrochloric acid concentration on heavy metal ion sorption on Lewatit VPOC 1065

The effect of hydrochloric acid concentration (0.1 – 6 M) on heavy metal ion sorption was examined ($C_0 = 20 \text{ mg/l}$), the results of which are depicted in **Figure 7**. With increasing HCl concentra-

tion, copper(II) sorption on both sorbents under discussion was not observed, whereas in the case of chromium(VI) the sorption capacity reduction was high, and in the system of 3 and 6 M HCl, sorption disappeared for both sorbents. Nickel(II) sorption on Lewatit VPOC 1065 was not HCl concentration dependent, whereas on titanium dioxide the sorption capacities increase with an increase in HCl concentration up to 1 M, then decrease (3 M HCl) and remain at the same level (6 M HCl). The effect of solution acidity on heavy metal ion sorption on ion exchange resins was previously observed [17, 19, 20]. With an HCl concentration increase, the total concentration of chloride ions also increases, the fraction of heavy metal species changes insignificantly, and competition between sorption sites can be observed.

Auxiliaries effect on AR183 sorption

Auxiliaries such as alkali, acids, salts, surface-active compounds, oxidants, reducing agents and thickeners are used in the chemical treatment of textiles. They constitute the main load for textile wastes and, apart from dyes, they remain in the sewage at a concentration close to the initial one. Only a small amount of auxiliaries settles on the textile product, because they do not wear out, creating proper conditions for the dyeing process. The average water consumption in all chemical fibre treatment processes is from about 150 to over 300 litres per 1 kilogram of fibre, resulting in the same amount of highly contaminated sewage [7].

In the present paper the influence of sodium chloride and sulfate, acetic acid as well as the anionic surfactant sodium dodecyl sulfate on AR183 sorption on Lewatit VPOC 1065 was studied. The amount of AR183 adsorbed by the

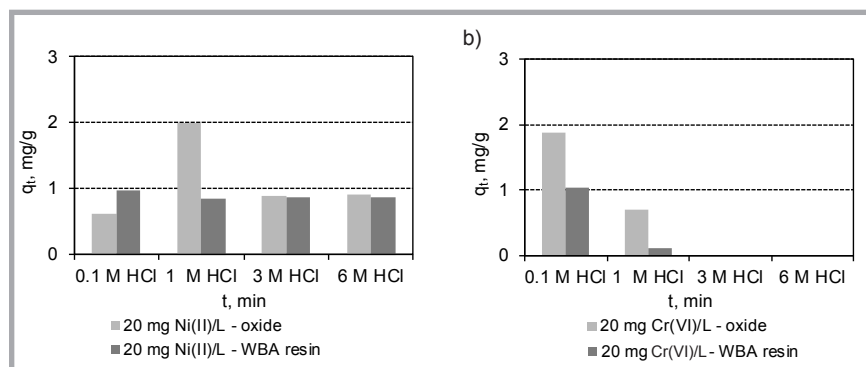


Figure 7. Effect of hydrochloric acid concentration on heavy metal ions sorption a) Ni(II), b) Cr(VI) on Adsorbisia™ As500 (oxide) and Lewatit VPOC 1065 (WBA resin).

weakly basic anion exchanger Lewatit VPOC 1065 after 15 min (q_t) from an aqueous solution of 500 mg AR183/l initial dye concentration was equal to 26.5 mg/g. The addition of NaCl to the above-mentioned system caused an insignificant drop in q_t values, as shown in Figure 8. However, the amount of NaCl added in the 5 – 50 g/l range had no significant effect on the value of q_t , which can be explained by the competitive sorption of chloride anions compared with the dye anions. The influence of sodium sulfate on AR183 sorption on Lewatit VPOC 1065 was reversed. The presence of Na_2SO_4 increased the q_t values up to 35.3 mg/g. The increase in q_t values is the result of the salt effect, which promotes dye sorption onto the matrix of the anion exchanger. The diverse effect of electrolytes on dye retention by weakly basic anion exchangers was previously described in paper [27].

After investigating AR183 sorption on Lewatit VPOC 1065 in an acetic medium (500 mg AR183/l – 0.5 – 2.5 g $\text{CH}_3\text{COOH}/\text{l}$), it can be stated that acetic acid increased the q_t values from 26.5 mg/g to 40.4 mg/g with an increase in CH_3COOH concentration up

to 2.5 g/l. As reported in the literature [27, 28], acetic acid did not usually influence or decrease the retention of acid dyes on the polystyrene anion exchangers.

A slight reduction in the amount of dye adsorbed by the polystyrene anion exchanger in the presence of the anionic surfactant SDS in the 500 mg AR183/L – 0.1 – 0.5 g SDS/l systems can be explained by its competitive sorption as compared with AR183 anions, especially noted in the case of C.I. Reactive Black 5 sorption on polystyrene anion exchangers of various basicity by Wawrzkiwicz and Hubicki [27].

Conclusions

The sorption efficiency of metal-complex dyes (AR183, RB21, NiPc-TSATSS) and heavy metal ions such as chromium(VI), nickel(II) and copper(II)) on titanium dioxide Adsorbisia™ As500 and the weakly basic anion exchanger Lewatit VPOC 1065 was compared. pH_{PZC} values of the sorbents were equal to 5.63 for Adsorbisia™ As500 and 2.45 for Lewatit VPOC 1065. The highest sorption capacity, $q_e = 816.1 \text{ mg/g}$, was found for AR183, and the selectiv-

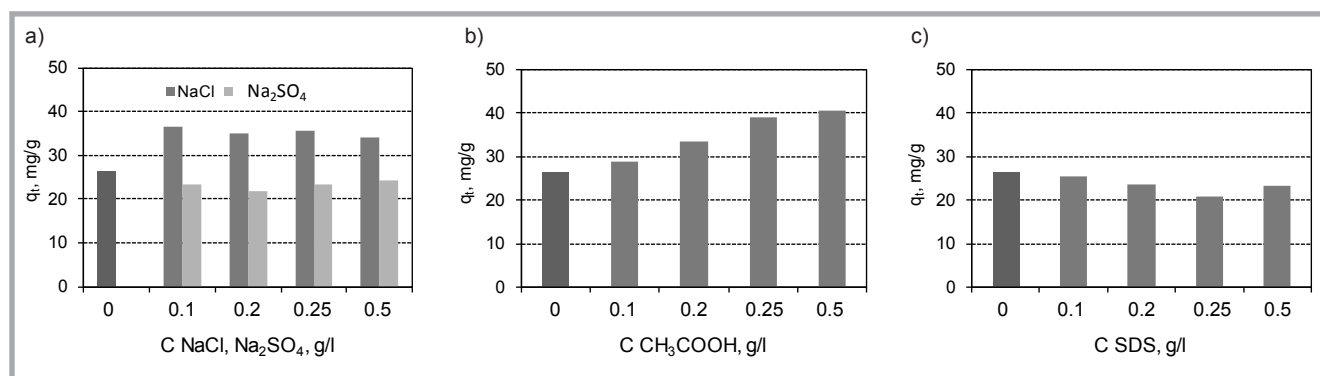


Figure 8. Effect of auxiliaries a) NaCl, Na_2SO_4 , b) CH_3COOH and c) SDS on AR183 sorption on Lewatit VPOC 1065.

ity series were as follows: Adsorbisia™ As500: RB21 > AR183 > Ni(II) > NiPc – TSATSS > Cr(VI) >> Cu(II), and Lewatit VPOC1065: AR183 > Cr(VI) > RB21 > Ni(II) > NiPc – TSATSS (8.8 mg/g) >> Cu (II). The WBA resin gives much higher or slightly higher % removal of toxic substances than titanium dioxide, and copper(II) sorption was not observed in the systems under discussion. The amount of toxic substances sorbed on Lewatit VPOC 1065 increases with the initial concentration and phase contact time. In the case of Cr(VI), a reduction in Cr(III) was observed. Toxic substance removal was fast from the solution of low initial sorbate concentration ($C_0 = 100$ mg/l) (equilibration time = 120 min, or > 240 min for higher C_0). The sorption yield of heavy metal ions was dependant on the solution acidity, whereas the sorption capacity for AR183 insignificantly dropped with the addition of NaCl in the 5 – 50 g/l range, increasing from 26.5 mg/g to 40.4 mg/g with an increase in CH₃COOH concentration to 2.5 g/l, and slightly decreasing with increasing SDS concentration.



Acknowledgements

The research presented was funded under a grant of the Ministry of Science and Higher Education for the development of young scientists and PhD students, BS-M-03-002-17-C-03.

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Received 17.11.2017 Reviewed 25.01.2018