Nature-like solution for removal of direct brown 1 azo dye from aqueous phase using humics-modified silica gel

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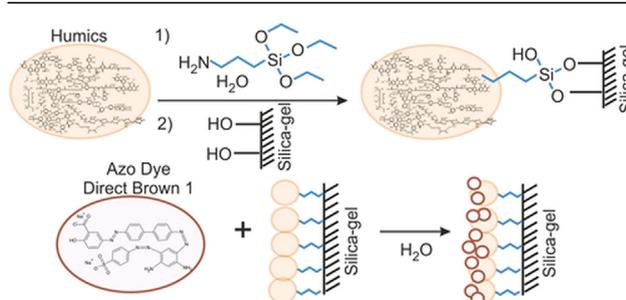[a] Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory 1-3, Moscow 119991, Russia
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HIGHLIGHTS

- Silanol humic derivatives are obtained by reaction with amino-organosilane in water.
- Silanol humic derivatives are immobilized onto silica gels using aqueous sorption.
- Humics-modified silica gels efficiently remove trisazo dye from aqueous phase.
- Similar approach can be used for removal of azo dyes released to aquatic environments.

GRAPHICAL ABSTRACT

ABSTRACT

The objective was to estimate suitability of humics-modified silica gels for adsorptive removal of the Direct Brown 1 trisazo dye from aqueous phase. The major advantage of the proposed adsorbents is that of an ecologically sound procedure of immobilizing silanized humic derivatives onto silica gel in aquatic solutions. The silanized humic derivatives, in turn, are obtained without a use of organic solvent by reacting natural humic materials from peat and coal with 3-aminopropyltriethoxyorganosilane in water. These silanized derivatives are surface active and are capable of self assembling into humic adlayers at the water solid interface. A use of this approach allows for immobilization of up to 220 mg of humic materials per 1 g of SiO_2. The adsorption capacity of humics-modified silica gels with respect to the Direct Brown 1 trisazo dye varied from 3.5 up to 8.8 mg per 1 g of SiO_2. The maximum sorption obtained for the silanized derivative with 50% modification degree was comparable to adsorption capacity of activated coal to this dye (7.5 mg g^{-1}). The results of this adsorption study, warrant further studies of azo dye removal from aqueous environments.

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1. Introduction

Azo dyes account for more than 50% of all the produced dyes (Chequer et al., 2011). As a result, they are the most common group of synthetic colorants released into the environment (Chung and

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Stevens, 1993; Maguire and Tkacz, 1991; Saratale et al., 2011; Solis et al., 2012). Many azo dyes and products of their degradation (e.g., aromatic amines) are toxic and expose mutagenic and carcinogenic effects on living organisms that raises serious environmental concerns (Mathieu-Denoncourt et al., 2014; Pereira and Alvis, 2012). Adsorption is one of the most effective processes of dye removal from contaminated water widely employed by industries (Allen and Koumanova, 2005; Babel and Kurniawan, 2003; McKay et al., 1980). Recent research has focused on developing cost-effective alternatives to activated carbon (Mohan et al., 2002; Yagub et al., 2014). Many have reported the feasibility of using various low cost adsorbents such as peat, lignite, clay, zeolites, coal fines, fly ash, different agricultural by-products and biosorbents (Crini, 2006; Gupta and Suhas, 2009; Mittal et al., 2013; Ong et al., 2007; Srinivasan and Viraraghavan, 2010).

In this context, the adsorption of pollutants by humic substances (HS) deserves specific attention (Perminova and Hatfield, 2005). HS are natural hyperbranched polyelectrolytes, which possess aromatic backbone highly substituted with functional groups. In nature, humic coatings attached to the surface of mineral particles engender higher sorption capacities for soils and sediments with respect to organic chemicals including azo dyes (Mathieu-Denoncourt et al., 2014; Olcay et al., 2009). This suggests that the immobilization of humic coatings onto surface of solid sorbents might increase substantially their sorption affinity for azo dyes. Indeed, in the prior work of Prado et al. (2003), it was reported that modification of silica gel with humic acid yielded sorbent with enhanced sorption capacity for removal of indigo carmene dye from aqueous phase. However, the process of sorbent preparation included treatment of silica gel with aminoorganosilane in toluene at 140 °C during 72 h, which makes the proposed procedure prohibitively expensive and ecologically not safe, while the prepared sorbent might contain traces of organic solvent.

The objective of this study was to propose a protocol of preparation of humics-modified silica gel suitable for azo dye removal from aqueous phase, which would be free of the above disadvantages. For this purpose, humic material is first reacted with aminoorganosilane in the aqueous phase; after which, the resultant silanized derivative is immobilized onto silica gel surface. Both reactions are carried out in aqueous phase that exclude residual contamination of the sorbent with organic solvent. Schematically the proposed approach is presented in Fig. 1.

Sorption properties of the prepared humics modified silica gel were demonstrated on azo dye Direct Brown 1. This dye was chosen as a representative of the sulfonated azo dyes which are highly water soluble and most refractory to biodegradation (Olcay et al., 2009).

2. Material and methods

2.1. Materials

Direct Brown 1 (C.I. 30045) azo dye belonging to direct application class and trisazo chemical class was employed as the test dye. Its molecular formula is $C_{31}H_{22}N_8Na_2O_6S$, and molecular weight is 680.615. Structural formula is shown in Supplementary Materials.

Direct Brown 1 was purchased from Sigma–Aldrich. Stock solution of the dye was prepared in MilliQ water at concentration of 200 mg/L. All other reagents used were of analytical reagent grade.

Two types of humic materials were used in this study. The first one was commercially available potassium humate (Sakhalin Humate) isolated from leonardite and designated as CHS. Peat sodium humate (PHS) was obtained from low moor peat by single extraction with 1 M NaOH. 3-aminopropyltriethoxysilane (APTES) was purchased from Penta Ltd. (Russia, Moscow). It was of technical-grade and used without further purification. Silica gel 60 was purchased from Merck and had specific surface area of 540 $m^2 \, g^{-1}$.

2.2. Functionalization of humic materials using APTES

A wide range of reagent ratios were used for modification of humic materials with APTES. The reaction stoichiometries were calculated on the basis of carboxyl group available in CHS and PHS. The content of carboxyl groups was determined using Ca-acetate method (Swift, 1996) and accounted for 2.7 and 2.9 mmol g^{-1} for CHS and PHS, respectively. Given that 1 g APTES contains 4.5 mmol of amine-groups, a 1:1 M ratio of COOH and NH_2 groups was reached by treating 1 g of CHS with 1.67 g (1.75 mL) of APTES. The reaction was run at three different APTES-to-humics molar ratios, nominally: 0.2, 0.5, and 1.0. These ratios corresponded to 20, 50, and 100% modification degree of carboxyl groups available within the humic backbone.

Prior to synthesis, a weight of potassium or sodium humate (CHS or PHS, respectively) was dissolved in distilled water in a beaker while stirring with a magnetic stirrer. A required aliquote of APTES was added dropwise to the obtained humate solution under continued stirring, and pH of the reaction mixture was adjusted to 4 with 5 M HCl. Then, the solution was transferred to a round bottom flask, and rotor-evaporated to dryness. The resulting products were stored in sealed vials. They looked like dark brown amorphous powders. The names of the samples obtained were constructed as CHS-APTES-X or PHS-APTES-X, where X is modification degree. In
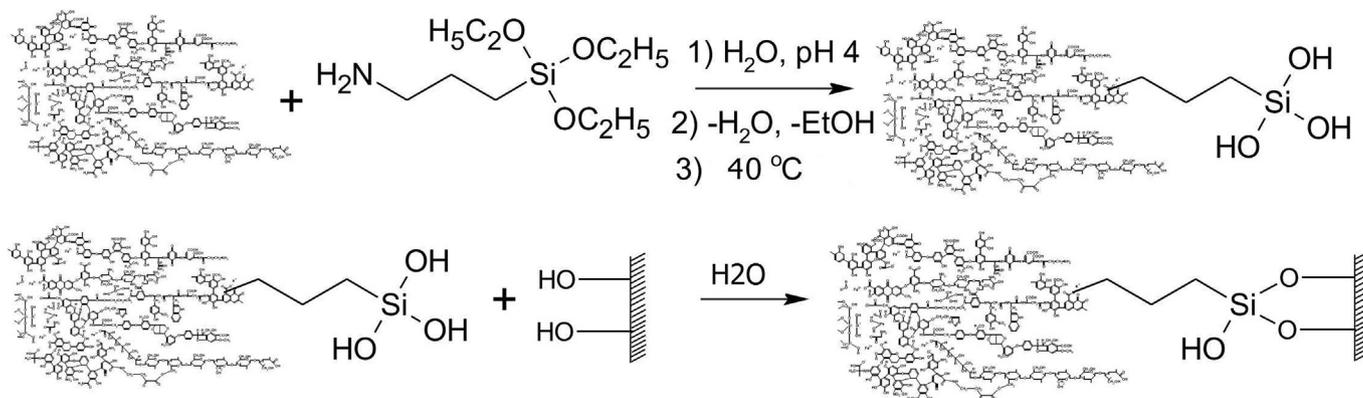

Fig. 1. Schematic reaction pathways for synthesis of silanized humic materials using 3-aminopropyltriethoxysilane (APTES) in aquatic medium and of their immobilization onto the silica gel surface in aqueous phase.

total, 3 samples were obtained for CHS and 3 samples − for PHS.

2.3. Characterization of the functionalized humic materials

Elemental analyses (C, H, N) were performed on Vario EL analyzer. The Si content was determined spectrophotometrically using *Specord M40*. Ash content was determined manually. Oxygen content was calculated as a difference. *Size Exclusion Chromatography (SEC)* analyses were conducted according to Perminova et al. (1998). The SEC column was 25 × 200 mm packed with Toyopearl HW-55S. Phosphate buffer (0.028 M, pH 6.8) was used as a mobile phase at a flow rate of 1 mL min^{-1}. The SEC column was calibrated using sodium polystyrenesulfonates (PSS), kDa: 14.0; 20.7; 45.1; and 80.84. Blue dextran (2000 kDa) served as a void volume probe, and acetone − as a permeation volume probe.

2.4. Sorption of silanol humic derivatives onto silica gel

Sorption experiments were conducted at room temperature (T = 22 ± 2 ^{O}C) in the presence of air on the day light using silica gel as sorbent. Solutions of humic materials at concentrations of 0.01−4 g L^{-1} were prepared by dissolving corresponding amounts of solid samples in several drops of concentrated NaOH and adjusting volumes to 10 mL with phosphate buffer (0.028 M, pH 6.0). An aliquot (10 mL) of each solution was added with 0.1 g of silica gel. Resulting suspensions were placed into an overhead-shaker for 1 day. To measure dissolved concentration of humic derivatives, the optical density of the solutions was monitored at 254 nm using UV−vis spectrometer (Cary 50, Varian Inc., U.S.A.). The calibration curves were plotted for each humic derivative used in this study to account for a substantial decrease in light absorbing capacities of the derivative along with an increase in its modification degree. This was an expected change due to an increase in aliphatic character of the highly modified humic materials. The amount of HS sorbed was calculated as shown below:

$$Q_{sorb.} = (C_0 − C_w) \, V/m, \tag{1}$$

where: $q_{sorb.}$ − amount of HS (mg) sorbed onto 1 g of silica gel (SiO$_2$), C_0 and C_w − initial and equilibrium concentration of HS in the solution (mg L^{-1}), reseptively, V − solution volume (mL), m − mass of silica gel (g).

2.5. Preparation of humics-modified silica gel sorbents for azo dye experiments

To prepare humics-modified silica gel sorbents, we used three silanol humic derivatives which showed the highest sorption affinity for silica gel (CHS-APTES-50, CHS-APTES-100, and PHA-APTES-100). The two former derivatives were obtained from coal humic materials, the latter one − from peat humic acid. An aliquot (100 mL) of the respective derivative at a concentration of 4 g L^{-1} was added to 1 g of silica gel in a 0.028 M phosphate buffer at pH 6.0 and then shaken for 48 h until sorption equilibrium was reached. Decreases in humic derivative concentration were monitored by measuring its UV-absorbance at 254 nm. The silica-gel was then centrifuged and washed repeatedly with distilled water. The product obtained was then dried in a vacuum desiccator over P$_2$O$_5$ for 48 h and labeled CHS-APTES-50-SiO$_2$, CHS-APTES-100-SiO$_2$, and PHA-APTES-50-SiO$_2$. The content of humic material in the resultant products was calculated from the measured loss of the derivative in solution. The content or organic carbon in the same products were determined from the data on elemental composition of the corresponding derivative.

2.6. Sorption of Direct Brown 1 onto silanol-humics treated silica gels

Sorption of Direct Brown azo dye on the modified silica gel was studied using equilibrium isotherm technique. The dye solutions were prepared in distilled water in the concentration range from 5 to 200 mg L^{-1}. The aliquotic parts of these dye solutions (10 mL) were placed into 15 mL centrifuge tubes containing 50 mg of silica gel (or modified silica gel) and agitated on the overhead shaker during 24 h. All experiments were run at 22 ± 2 °C. Then, the suspensions were centrifuged and the supernatant was analyzed for dye content by measusring its optical density at 380 nm. The sorbed amount of the dye (Q$_{sorb}$) was calculated using same equation as in case of HS (1).

3. Results and discussion

Modifications of coal and peat humates (CHS and PHS, respectively) with organosilane were carried out in water. This is a principal difference to our prior works (Karpiouk et al., 2012; Perminova et al., 2012) where we demonstrated feasibility of efficient silanization of humic materials in dimethyl formamide (DMF), but searched instantly for alternative to this solvent to avoid contamination of the final product. Here we propose a solution to this problem by using water as a solvent and amine-functionalized organosilane (e.g. 3-aminopropyltriethoxysilane (APTES)) for the purpose of modification. Rationale behind was that amine group of organosilane does not react with water, but it is capable of binding to abundant carboxyl-groups of humic materials dissolved in water yielding surface active humic derivatives functionalized with silanol groups. The corresponding modifications were carried out at three different molar ratios of APTES to HS varying from 0.2 up to 1.0 on the basis of carboxylic acidity of the initial humic material. Surface activity of the silanized derivatives was characterized using equilibrium sorption onto silica gel. The corresponding sorption isotherms are shown in Fig. 2. The obtained derivatives were also characterized by data on their elemental compositions, carboxyl group content, and molecular weight characteristics. Together with sorptive characteristics, they are given in Table 1.

The obtained isotherms show clearly that modification of the both humic materials used in this study with APTES enhances drastically their sorption capacity for silica gel: it starts from zero sorption in case of initial humic materials (CHS-K and PHS-Na) and ends up with 200 mg g^{-1} for the same humic material silanized with APTES at 100% modification degree. These data are comparable with sorption affinity of the alkoxysilyl-derivatives of humic materials obtained in organic solvent (Perminova et al., 2012) and exceed sustantially the reported data on sorption capacity of the aminized silica gels with respect to humic acids (80 mg HS·g^{-1} SiO$_2$) (Prado et al., 2003).

Given that the isotherms from Fig. 2 are S-type and do not plateau even at maximum concentrations used in this study, they were characterized with point values of maximum sorption (Q$_{max}$) and distribution coefficient K$_d$. The former was calculated as a sorption of HS in mg per 1 g of SiO$_2$ at the maximum HS concentration of 4 g L^{-1}, and the latter was determined at the same concentration of HS. The corresponding data are presented in Table 1.

It can be deduced from Table 1 that the amount of Si gradually increased with increasing rates of APTES in the reaction mixtures indicating progressive modification of HS. This trend was followed by an increase in C/N ratio indicative of the contribution of nitrogeneous organosilane into humic structure, and by a decrease in the content of free carboxyl groups in the modified humic materials. Molecular weight characteristics of the silanized derivatives indicate an increase in weight average molecular weight (M$_w$) and
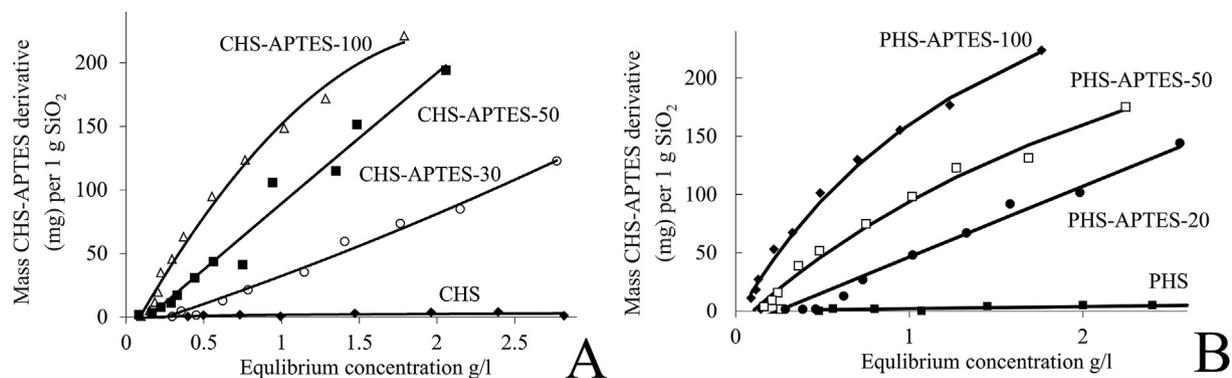
Fig. 2. Sorption isotherms of the silanized derivatives of coal humic substances (CHS) (A) and peat humic substances (PHS) (B) onto silica-gel. Sorption conditions: 0.028 M phosphate buffer, pH 6.0, 0.1 g SiO$_2$ per 10 mL of HS solution, equilibrium time 24 h, T = 22 ± 2 °C.

Table 1
Structural, molecular weight, and sorption characteristics of the humic materials.

Name	C, %	Si %	H/C	C/N	COOH, mmol g^{-1}	M$_w$, kDa	M$_w$/M$_n$	Q$_{max}$,[a] mg HS g^{-1} SiO$_2$	K$_d$,[b] L g^{-1}
CHS	31.7	6.3	1.08	0.04	2.7 ± 0.1	12.7	3.6	1	0.59
CHS-APTES-20	32.4	6.4	0.9	0.05	2.4 ± 0.4	16.9	5.4	30	27
CHS-APTES-50	31.6	7.5	1.34	0.08	2.0 ± 0.3	28.8	3.2	194	69
CHS-APTES-100	31	8.8	1.21	0.11	1.8 ± 0.4	26.3	10.2	221	170
PHS	40.9	0.6	1.2	0.08	2.9 ± 0.2	28.7	4.5	1	0.48
PHS-APTES-20	40.1	2.1	1.3	0.09	2.2 ± 0.4	26.3	4.5	144	36
PHS-APTES-50	38.8	4.4	1.33	0.11	2.4 ± 0.4	27.8	4.5	175	107
PHS-APTES-100	31.4	5.5	1.46	0.14	1.7 ± 0.4	62.8	7.6	223	205

[a] Q$_{max}$ is a sorption value of HS in mg per 1 g of SiO$_2$ at HS concentration of 4 g L^{-1}.
[b] K$_d$ is a ratio of the HS equilibrium concentration in solution to the sorbed HS in mg per 1 g of SiO$_2$ at an initial concentration of humic derivatives 4 g L^{-1}.
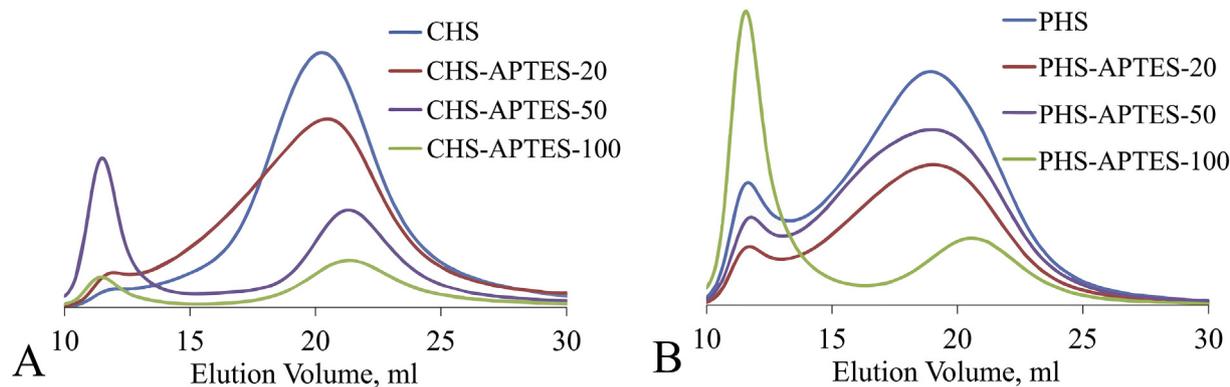

Fig. 3. SEC chromatograms of CHS (A), PHS (B) and their silanized derivatives. The SEC column was 25 × 200 mm packed with Toyopearl HW-55S. Phosphate buffer (0.028 M, pH 6.8) was used as a mobile phase at a flow rate of 1 mL min^{-1}.

polydispersity (M$_w$/M$_n$) values of the derivatives along with an increase in modification degree. Inspection of the corresponding SEC chromatograms (Fig. 3) shows that the more substantial shift towards higher molecular weight was characteristic for the CHS derivatives as compared to the PHS derivatives. This could be connected to the lower molecular weight of the parental coal HS (12.7 kDa) versus much heavier PHS (28.7 kDa).

The intense peak at the void volume of the column might be connected to formation of colloidal matter in the solutions of silanized derivatives with higher modification degree which is excluded at the void volume of the column. Supposedly, this colloidal matter is silica sol formed as a result of partial hydrolysis of the silane residues within humic derivatives.

Structural alterations in APTES-modified HS were characterized

using FTIR spectroscopy on the example of CHS-APTES-100 derivative. FTIR spectra of the parental coal HS (potassium humate, CHS-K) and APTES are given for comparison (Fig. 4).

The typical FTIR spectrum of the silanized derivative is characterized by appearance of two strong absorption bands of Si–O–C bonding at 1100 and 1050 cm^{-1}, which can be also seen in the spectrum of APTES. The sharp peak of carboxylate positioned at 1560 cm^{-1} in the spectrum of parental humate (CHS-K), has broadened up to 1640 cm^{-1} in the spectrum of CHS-APTES-100, which is indicative of large contribution of amide >C=O (amide I) usually located at 1630–1695 cm^{-1}. The presence of amide bond is also confirmed by high peak intensity at 1560 cm^{-1} (amide II and carboxylate) and a weak band at 1265 cm^{-1} (amide III). The similar changes were observed for all APTES-HS derivatives. They can
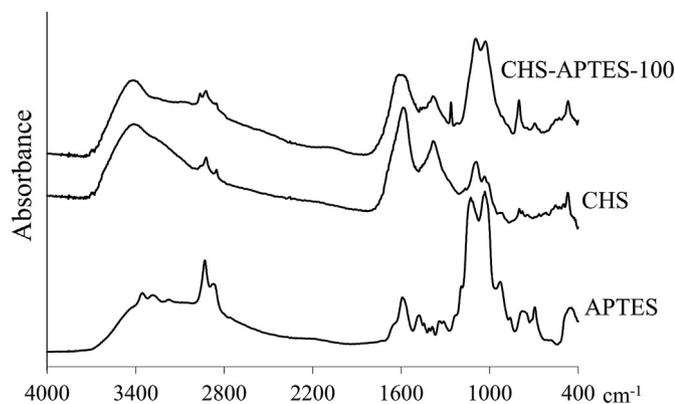
Fig. 4. FTIR spectra of the parental coal HS (potassium humate, CHS), APTES, and the CHS-APTES-100 derivative.

indicate that attachment of APTES to HS in aquatic solutions occurs both via covalent bonding and ionic interaction of protonated aminoorganosilane with negatively charged polyanions of HS. This also explains the presence of residual carboxyl groups in the silanized derivatives with the highest modification degree (Table 1). Despite of that, the obtained derivatives are characterized with the same high maximum values of sorption capacity (220 mg HS$\cdot$g^{-1} SiO$_2$) as those reported for the silanized derivatives synthesized in organic solvent (Karpiouk et al., 2012). These values are comparable with the content of HS in the organic rich geosorbents − mollisols, sediments, and others.

To estimate efficacy of the humics-modified silica gels obtained with a use of the proposed approach for azo dye removal from aqueous phase, we used batch experimental set up. Direct Brown 1 was used as a representative of sulfonated azo dyes which are the most problematic for water treatment and remediation due to their high solubility in water, low retardation, and stability towards biodegradation (Ali, 2010; Yagub et al., 2014). Silica gels used for this experiment were obtained by modification with the silanized humic derivatives which showed maximum sorption capacity onto SiO$_2$ (Table 1): CHS-APTES-50, CHS-APTES-100, and PHS-APTES-100. Modification of silica gel was conducted in the concentrated solution of the corresponding humic derivative (4 g L^{-1}), which enabled immobilization of the largest amount of humic material. Desorption experiments run on thus modified silica gels have shown irreversible sorption of the silanized humic materials onto silica gel: there was no bleaching observed of the sorbed humic material upon multiple washing of the modified silica gels with
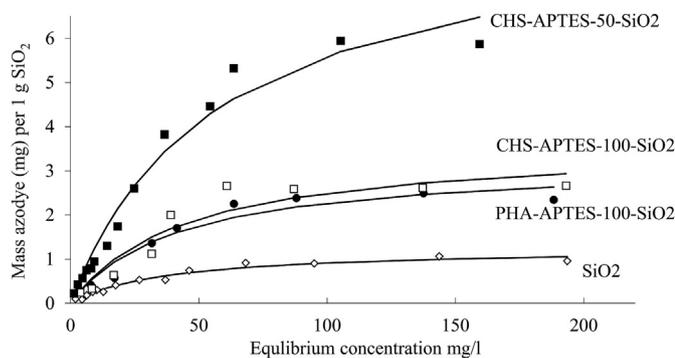

Fig. 5. Sorption of Direct Brown 1 trisazo dye onto silica gel modified with coal humic derivatives (CHS-APTES-50 and CHS-APTES-100) and peat humic derivative (PHA-APTES-100). T = 22 ± 2 °C, pH = 6.0, distilled water. Solid to liquid ratio: 100 mg SiO$_2$ per 10 mL of dye solution.

both 0.028 M phosphate buffer and distilled water (the data are not shown).

Equilibrium sorption isotherms of the Direct Brown 1 azo dye onto the humics-modified silica gels are shown in Fig. 5. The amount of the sorbed dye was determined from a decrease in optical density of the solution at 390 nm which was used for monitoring adsorptive removal of the dye. The obtained isotherms are of L-type and fit well to Langmuir model.

From the obtained data it can be concluded that much higher adsorptive removal of the dye was observed onto humics-modified silica gels as compared to non-modified silica gel. At the same time, among the humics-treated silica gels the highest efficacy was characteristic to the silica gel treated with humic derivative of the lowest modification degree - CHS-APTES-50. The value of maximum sorption reached onto this sorbent (8.8 mg g^{-1}) exceeded those (in mg g^{-1}) onto coal based sorbents such as lignite coal (4.1), bituminous coal (2.04), charfines (6.4), and activated carbon (7.69 mg g^{-1}) as reported by Mohan et al. (2002) under comparable experimental conditions. This makes the developed sorbent of substantial interest for a use in removal of azo dyes from aqueous phase.

The lower sorption capacity of Direct Brown azo dye onto the both silica gels treated with the silanized humic derivatives of 100% modification degree (3.2 and 3.6 mg per g of SiO$_2$ for CHS-APTES-100 and PHS-APTES-100, respectively) can be explained by a substantial decrease in the pore volume of the treated silica gel due to deposition of the colloidal silica released as a result of hydrolysis of the silanol derivatives which intensifies along with an increase in HS:APTES ratio. This is consistent with the SEC-results (Fig. 3) and with the data of BET measurements which showed a substantial decrease in pore volume of the silica gel at the highest loadings with the humic material. Hence, derivatives of smaller modification degree are preferrable for modification of silica gel. This also complies well with optimization of the expenses for preparing modified silica gel because of a reduced amount of organosilane needed to react with natural humic material.

The proposed approach can be realized in two different ways: the first one implies preparation of the humics-coated silica gel as described in this study, without a use of organic solvent, followed by its deployment as a sorbent in columns or in slurries for removing dye from waste water effluents similar to silica gels, coal-based and other low cost adsorbents (McKay et al., 1980; Mohan et al., 2002; Gupta and Suhas, 2009); the second one includes in situ deployment of the solutions of silanolized humics for cleaning up dye-contaminated ground water by pumping them into the aquifer. In the second case, the removal of dye from groundwater occurs via its sorption onto humic adlayer which is self-assembled at the water−solid interface and attached to granular aquifer support via Si−O−Si linkages (Karpiouk et al., 2012; Perminova et al., 2012). The first deployment strategy is most suitable for off-site wastewater cleanup, whereas the second strategy might be deployed on site through in situ installation of the humic permeable reactive barriers.

In case of the first strategy, regeneration of the humics-modified silica-sorbents might be needed. It can be achieved via treatment with diluted solutions of KOH or NaOH (0.01 M) similar to the protocols reported for chitosan-based sorbents loaded with the anionic diazo-dyes (Shen et al., 2011; Szygula et al., 2008). This treatment will recycle silica gel by removing humic adlayer with the sorbed azodye. The dye bearing humic waste can be easily compacted by acidification and separation of the humic-dye precipitate, which can be incinerated or biodegraded (Yagub et al., 2014). The regenerated silica gel can be re-modified with silanolized humics and reused for the next cycle. The advantage of using the proposed environmental solutions stems from ecological

safety of humics-based materials and richness of their low-cost reserves such as lignites, lignins, composts, etc.

4. Conclusion

The nature-inspired appoach is proposed to adsorptive removal of the Direct Brown azo dye from aqueous phase based on a use of humics-modified silica gels. The major novelty of this approach is that modification of silica gel was conducted in water by using surface-active silanized humic materials. The latter are natural hyperbrached polyelectrolytes capable of both ionic, hydrophobic, and donor—acceptor interactions due to the presence of numerous functional groups and amphiphilic properties of their structures. As a result, humic adlayers can efficiently adsorb not only azo dyes present in the effluent but concomittant contaminants, such as heavy metals and other organic chemicals, as well. The humic adlayers can also serve as a solid support and redox shuttles for azo dye degrading microorganisms (Cervantes et al., 2001; Hong et al., 2007) which increases an added value of their use in dye removal and remediation processes (Martínez et al., 2013). Another advantage of the proposed approach is that the silanized humic derivatives can be also employed in situ (e.g., injected into contaminated aquifer) for creating humic adlayers onto granular support. Recently, we have demonstrated feasibility of this approach for removal of plutonium (Shcherbina et al., 2014). To show its applicability for waters contaminated with azo dyes is our nearest goal.

Acknowledgments

Supplementary materials

Structural formula of Direct Brown 1 azo dye, BET-measurements and linearized isotherms for the Direct Brown 1 trisazo dye adorption onto modified silica gels are available for this paper.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2015.11.070.

References

Allen, S.J., Koumanova, B., 2005. Decolourisation of water/wastewater using adsorption (review). J. Univ. Chem. Technol. Metall. 40 (3), 175—192.

Ali, H., 2010. Biodegradation of synthetic dyes — a review. Water Air Soil Pollut. 213 (1), 251—273.

Babel, S., Kurniawan, T.A., 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. J. Hazard. Mater 97 (1—3), 219—243.

Chung, K.T., Stevens, S.E.J., 1993. Degradation of azo dyes by environmental microorganisms and helminths. Environ. Toxicol. Chem. 12 (11), 2121—2132.

Cervantes, F.J., van der Zee, F.P., Lettinga, G., Field, J.A., 2001. Enhanced decolourisation of acid orange 7 in a continuous UASB reactor with quinones as redox mediators. Water Sci. Technol. 44, 123—128.

Chequer, F.M.D., Dorta, D.J., de Oliveira, D.P., 2011. Azo dyes and their metabolites: does the discharge of the azo dye into water bodies represent human and ecological risks? In: Hauser, P.J. (Ed.), Advances in Treating Textile Effluent. InTech Publisher, pp. 27—48. ISBN 978-953-307-704-8.

Crini, G., 2006. Non-conventional low-cost adsorbents for dye removal: a review. Bioresour. Technol. 97 (9), 1061—1085.

Gupta, V., Suhas, C.P.J.M., 2009. Application of low-cost adsorbents for dye removal—a review. J. Environ. Manag. 90 (8), 2313—2342.

Hong, Y.G., Guo, J., Xu, Z.C., Xu, M.Y., Sun, J.P., 2007. Humic substances act as electron acceptor and redox mediator for microbial dissimilatory azoreduction by Shewanella decolorationis S12. J. Microbiol. Biotechnol. 17 (3), 428—437.

Karpiouk, L.A., Ponomarenko, S.A., Mourran, A., Bochkariov, D., Muzafarov, A.M., Hatfield, K., Perminova, I.V., 2012. Self assembly of alkoxysilanized humic substances into multidomain adlayers at water-solid interface: linking surface morphology to molecular structures of adsorbate. Soft Matter 8 (8), 2452—2459.

Maguire, R.J., Tkacz, R.J., 1991. Occurrence of dyes in the Yamaska river, Quebec. Water Pollut. Res. J. Can. 26 (2), 145—161.

Martínez, C.M., Celis, L.B., Cervantes, F.J., 2013. Immobilized humic substances as redox mediator for the simultaneous removal of phenol and reactive red 2 in a UASB reactor. Appl. Microbiol. Biotechnol. 97, 9897—9905.

Mathieu-Denoncourt, J., Martyniuk, C.J., de Solla, S.R., Balakrishnan, V.K., Langlois, V.S., 2014. Sediment contaminated with the azo dye disperse yellow 7 alters cellular stress- and androgen-related transcription in Silurana tropicalis larvae. Environ. Sci. Technol. 48, 2952—2961.

McKay, G., Otterburn, M.S., Sweeney, A.G., 1980. The removal of colour from effluent using various adsorbents—III. Silica: rate processes. Wat. Res. 14, 15—20.

Mittal, J., Thakur, V., Mittal, A., 2013. Batch removal of hazardous azo dye Bismark brown R using waste material hen feather. Ecol. Eng. 60, 249—253.

Mohan, S.V., Rao, N.C., Karthikeyan, J., 2002. Adsorptive removal of direct azo dye from aqueous phase onto coal based sorbents: a kinetic and mechanistic study. J. Hazard. Mater 90, 189—204.

Olcay, T., Dindar, E., Uçaroğlu, S., Baskaya, H.S., 2009. Effect of a sulfonated azo dye and sulfanilic acid on nitrogen transformation processes in soil. J. Hazard. Mater 170, 1006—1013.

Ong, S., Lee, C., Zainal, Z., 2007. Removal of basic and reactive dyes using ethylenediamine modified rice hull. Bioresour. Technol. 98 (15), 2792—2799.

Pereira, L., Alvis, M., 2012. Dyes-environmental impact and remediation. Ch. 4. In: Malik, A., Grohmann, E. (Eds.), Environmental Protection Strategies for Sustainable Development, Strategies for Sustainability. Springer Science+Business Media B.V., pp. 112—163. http://dx.doi.org/10.1007/978-94-007-1 591-2_ 4

Perminova, I.V., Frimmel, F.H., Kovalevskii, D.V., Abbt-Braun, G., Kudryavtsev, A.V., Hesse, S., 1998. Development of a predictive model for calculation of molecular weight of humic substances. Wat. Res. 32, 872—881.

Perminova, I.V., Hatfield, K., 2005. Remediation chemistry of humic substances: theory and implications for technology. In: Perminova, I.V., Hatfield, K., Hertkorn, N. (Eds.), Use of Humic Substances to Remediate Polluted Environments: from theory to practice, NATO Science Series: IV: Earth and Environmental Sciences, 52. Springer, Dordrecht, The Netherlands, pp. 3—36.

Perminova, I.V., Karpiouk, L.A., Ponomarenko, S.A., Konstantinov, A.I., Hertkorn, N., Hatfield, K., 2012. Controlling aqueous sorption of humic substances on silica gel by directed alkoxysilyl-derivatization of their functionalities. Colloids Surf. A 396, 224—232.

Prado, A.G.S., Miranda, B.S., Jacintho, G.V.M., 2003. Interaction of indigo carmine dye with silica modified with humic acids at solid/liquid interface. Surf. Sci. 542, 276—282.

Saratale, R.G., Saratale, G.D., Chang, J.S., Govindwar, S.P., 2011. Bacterial decolorization and degradation of azo dyes: a review. J. Taiwan Inst. Chem. Eng. 42 (1), 138—157.

Shcherbina, N.S., Kalmykov, S.N., Karpiouk, L.A., Ponomarenko, S.A., Hatfield, K., Haire, R., Perminova, I.V., 2014. Non-reversible immobilization of water-borne plutonium onto self-assembled adlayers of silanized humic materials. Environ. Sci. Technol. 48 (4), 2226—2233.

Shen, C., Shen, Y., Wen, Y., Wang, H., Liu, W., 2011. Fast and highly efficient removal of dyes under alkaline conditions using magnetic chitosan-Fe(III) hydrogel. Water Res. 45, 5200—5210.

Solis, M., Solis, A., Perez, H.I., Manjarrez, N., Flores, M., 2012. Microbial decolouration of azo dyes: a review. Process Biochem. 47 (12), 1723—1748.

Srinivasan, A., Viraraghavan, T., 2010. Decolorization of dye wastewaters by biosorbents: a review. J. Environ. Manage 91, 1915—1929.

Swift, R.S., 1996. Organic matter characterization (Chap 35). In: Methods of Soil Analysis. Soil Science Society of America, Madison, WI, pp. 1018—1020. Part 3.

Szygula, A.M., Ruiz, M., Guibal, E., Sastre, A.M., 2008. Removal of an anionic reactive dye by chitosan and its regeneration. In: Mastorakis, N.E., Poulos, M., Mladenov, V., et al. (Eds.), Waste Management, Water Pollution, Air Pollution, Indoor Climate. WSEAS Press, pp. 24—30. ISBN: 978-960-474-017-8.

Yagub, M.T., Sen, T.K., Afroze, S., Ang, H.M., 2014. Dye and its removal from aqueous solution by adsorption: a review. Adv. Colloid Interface Sci. 209, 172—184.