Sorption of Acid Yellow 23 from aqueous solutions onto soil

Florentina Anca Caliman^{1*}, Laura Carmen Apostol¹, Dumitru Bulgariu^{2,3}, Laura Bulgariu¹ Maria Gavrilescu¹

¹"Gh. Asachi" Technical University of Iasi, Faculty of Chemical Engineering & Environmental Protection, Department of Environmental Engineering & Management, 71 A, D. Mangeron Blvd., 700050 Iasi, Romania ²"Al.I.Cuza" University of Iasi, Faculty of Geography and Geology, Department of Geology and Geochemistry, 20 A, Carol I Blvd. 700506, Iasi, Romania ³Romanian Academy, Filial of Iasi, Collective of Geography, 18 Carol I Blvd, 700506, Iasi, Romania

> Sorción de tartrazina de soluciones acuosas por el suelo Sorció de tartrazina de solucions aquoses pel sòl

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RESUMEN

La tartrazina, un colorante azoico aniónico, también conocido como Acid Yellow 23, Amarillo FD&C 5, CI 19140 o E102 (a Europa), es ampliamente utilizado en medicina y cosmética, así como en las industrias alimentaria y textil. En los productos farmacéuticos, la tartrazina se incorpora como aditivo en medicinas, antiácidos y suplementos vitamínicos, mientras que en cosmética se usa en tintes capilares, jabones, lociones, champúes, geles de baño, cremas para la piel, desodorantes, barras de labios y muchas otras aplicaciones. Dado que se utiliza ampliamente con diversos propósitos, la tartrazina se puede encontrar con frecuencia en las aguas residuales municipales y en las aguas residuales provenientes de la industria textil, alimentaria, farmacéutica y cosmética. En este contexto, puede resultar también en un impacto negativo sobre el medio ambiente por vertido de aguas residuales inadecuadamente tratadas. En este trabajo, se investiga la capacidad de un suelo de Rumania para retener la tartrazina en solución acuosa mediante sorción. Se aplican los modelos de Freundlich, Langmuir y de la isoterma lineal para describir el proceso, y se calculan los parámetros de estas ecuaciones. Se investiga la cinética de la sorción aplicando cinco modelos cinéticos con objeto de establecer el modelo que mejor se ajusta al proceso de sorción de los colorantes azoicos por las partículas del suelo investigado.

Palabras clave: Tartrazina, colorantes azoicos, suelo, sorción

ABSTRACT

Acid Yellow 23, an anionic azo dye, also known as Tartrazine, FD&C Yellow 5, CI 19140 or E102 (in Europe) is widely used in medicine or cosmetics, foodstuff and textile industries. In pharmaceuticals, Acid Yellow 23 is incorporated as additive in medicines, antacids, vitamin supplements, whereas in cosmetic industries, it is utilized in hair dyes, soaps, lotions, shampoos, bath gels, skin-care creams, deodorants, lipsticks and many others. Due to its very wide use for different purposes, Acid Yellow 23 may be commonly found in municipal wastewaters or wastewaters originating from textile, food, drugs and cosmetic industry. In this context, it may also result in negative impact on the environment through discharge of improperly treated wastewaters in receiving waters. In this work, the capacity of a Romanian soil to retain Acid Yellow 23 from aqueous solution by sorption has been investigated. The Freundlich, Langmuir and linear isotherm models were applied to describe the process and the parameters of these equations were calculated. The sorption kinetics was investigated by applying five kinetic models aiming at establishing the model that best fits the sorption of the azo dyes onto the particles of investigated soil.

Keywords: Acid Yellow 23, azo dyes, soil, sorption

RESUM

La tartrazina, un colorant azoic aniònic, també conegut com Acid Yellow 23, Groc FD&C 5, Cl 19140 o E102 (a Europa) és amplament utilitzat en medicina i cosmètica, així com a les indústries alimentària i tèxtil. En els productes farmacèutics, la tartrazina s'incorpora com a additiu a medicines, antiàcids i suplements vitamínics, mentre que en cosmètica s'empra en tints capil·lars, sabons, locions, xampús, gels de bany, cremes per a la pell, desodorants, barres de llavis i moltes altres aplicacions. Donat que s'empra amplament amb diferents propòsits, la tartrazina es pot trobar sovint a les aigües residuals municipals i a les aigües residuals provinents de la indústria tèxtil, alimentària, farmacèutica i cosmètica. En aquest context, pot resultar també en un impacte negatiu sobre el medi ambient per abocament d'aigües residuals inadequada-

*Corresponding author: acali@ch.tuiasi.ro

ment tractades. En aquest treball, s'investiga la capacitat d'un sòl de Romania per retenir la tartrazina en solució aquosa mitjançant sorció. S'apliquen els models de Freundlich, Langmuir i de la isoterma lineal per descriure el procés, i es calculen els paràmetres d'aquestes equacions. S'investiga la cinètica de la sorció aplicant cinc models cinètics per tal d'establir el model que millor s'ajusta al procés de sorció dels colorants azoics per les partícules del sòl investigat.

Mots clau: Tartrazina, colorants azoics, sòl, sorció

1. INTRODUCTION

Acid Yellow 23 (Tartrazine), a water-soluble anionic colorant, can be used in a wide variety of applications, including the coloring of a large number of pharmaceuticals and personal care products, but is also a food additive¹⁻⁴. Thus, Acid Yellow 23 is incorporated as additive in certain prescription drugs, antacids, vitamin supplements, whereas in cosmetic industries, it is utilized in hair dyes, soaps, lotions, shampoos, bath gels, skin-care creams, deodorants, lipsticks and many others. Acid Yellow 23 is listed as CI 19140 in Annex IV, part 1 of Directive 76/768/EEC – list of colorings agents allowed for use in cosmetic products and is proposed to be used as a hair coloring agent (direct dye) in semipermanent hair dye formulas at a maximum concentration of 0.5% in the finished cosmetic product.

Acid Yellow 23 is permitted also as a food colorant (E102) in the EU. It is listed in the priority based Assessment of Food additives for use in the USA, as well. The Joint Food and Agriculture Organization - World Health Organization Expert Committee on Food Additives (JECFA) and the Scientific Committee of Food have set an acceptable daily intake (ADI) of 7.5 mg Kg⁻¹ for this dye⁵.

Acid Yellow 23 is suspected to constitute a real danger for human health resulting in deficiencies in zinc and vitamin B6 and even in appearance of tumors, especially in women. This is due to fact that B6 is involved in the metabolism of progesterone that, in its turn has an important role in processing the excess of estrogen. In this way, the women exhibiting hormonal problems (estrogen hyper secretions) may develop different types of tumors in time⁶. Moreover, this dye is also suspected to cause depression, anxiety, infertility and migraines to adults and hyperactivity disorders to children⁷.

Other possible adverse effects of Acid Yellow 23 refers to the fact that it⁸:

causes allergic reactions;

is involved in induction of asthma;

produces adverse food reactions involving immune mechansimas such as urticaria;

leads to non-imunnological reactions as bronhospasm in asmathic aspirin-intolerant individuals.

As a result of the negative impact that this pollutant may exert onto human health and ecosystems, it was banned in Norway, Austria and Germany, whereas in other several countries it is used with some restrictions. However, its many commercial names may be used to avoid these restrictions. Hence, Tartrazine is named as Acid Yellow 23 on hair dying products labels, but is specified as CI 19140 when is used as colorant in other cosmetic products. While no restrictions are stated in the first case, it must obey the conditions laid down in the Annex IV of the EU Cosmetic Directive (Council Directive 76/768/EEC), in the second case⁹.

Due to its very wide use for different purposes, Acid Yellow 23 may be commonly found in municipal wastewaters or wastewaters originating from textile, food, drugs and cosmetic industry. In this context, it may also result in negative impact on the environment through discharge of improperly treated wastewaters in receiving waters. For this reason, the removal of Acid Yellow 23 from wastewater is highly requested, numerous studies being focused on the possibility to remove this dye by sorption onto low-cost, accessible and environmental-friendly sorbents as clays¹⁰, bentonite¹¹, bottom ash and de-oiled soya¹², hen feathers¹³, but also degradation by different advanced oxidation methods is investigated¹⁴⁻¹⁸.

In this work, the capacity of the soil sampled from the lasi area (city situated in the north-eastern part of Romania) to retain Acid Yellow 23 from aqueous solution by sorption has been investigated.

In the region of lasi County, the soils, especially those from the northern part are mainly represented by chernozems formed through strong bioaccumulation process occurring in an excessive continental temperate climate, whereas in the southern part, the main factors of pedogenesis are¹⁹:

land forms formed by soil layering in order haplic chernozems-luvic chernozems-haplic luvisols;

geomorphologic processes that alter the soil distribution.

In the eastern, central-eastern and central western compartments, soils were formed onto alluvial parental materials (fluvisols) under the shape of bands within the Bahlui and Jijia flood plains. The preponderant clayey texture of the flood plain soils, alongside the low longitudinal declivity and the water flow on the north-facing slope bordering Bahlui River as well as on the level of the right slope of Jijia River favor the association of the gleyic or stagnic-gleyic processes with the fluvisols.

Human actions influence the pedological cover through changing the profile of soil morphology as a result of the industrial activities or of intensive use of land for agriculture. Industrial activities and especially those connected to civil construction contribute to appearance of new parental materials due to inclusion of brick fragments, concrete, glass etc within the soil profile, which allowed the urbic anthroslos to be distinguished. In comparison to the residential areas dominated by houses with yards and gardens (Sararie, Copou), the most affected soils are those in the districts with blocks of flats (Nicolina, Galata, Alexandru cel Bun). In the perimeter of the industrial areas, the soils contain specific, highly non-biodegradable wastes as, for example, slag fragments in the Fortus SA area. Allocchthonous rock fragments are frequently found in the soil profile of areas of transport activities such as lasi Railway Station, where on small spots may be found skeletic regosols, but owing to the difficult cartographic representation, these can have been assimilated to regosols. Domestic wastes as Tomesti waste dump contribute to formation of garbic regosols. Deep changes in soil profile due to agro-technical processing is specific to the slopes covered with orchards and vineyards as are the eastfacing slope Sorogari Hill and the west-facing slopes of Breazu Hill. In general, the sunny slopes are covered

Table 1. General characteristics of the soil samples

Soil type/ subtype	Protisoil (litosoil)/ Urbic regosol associated with molic-gleyc / pelic fluvisol	
Structure*	Medium / loam sand	
Anthropogenic modification	Intense	
Pollution**	Weak-medium	
pH	5.88	
E _h	580.13	
CECt	10.61	

*Concordant to the Romanian System of Soil Taxonomy (SRTS-2003); **Concordant to literature^{20,21}; *E_h* – redox potential (mV); CEC_t – total cationic exchange capacity (mequiv. / 100 g soil)

Table 2. Chemical and minerald	ogical components of the so	oil samples (%, w / w)*
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	Smectite		15.29	
Clay minerals (%, w /w)	Illite		9.87	
	Kaolinite		19.20	
	Amorphous		3.24	
	Total		47.62	
Carbonates	Total (%, w / w)		4.86	
	Crystalline		1.50	
Iron oxides and oxyhydroxides (%, w/w)	Amorphous		2.04	
	Total		3.54	
Silica (SiO ₂) (%, w / w)	Crystalline		6.64	
	Amorphous		4.42	
	Total		11.06	
Other minerals	s** (%, w / w)		6.13	
	Humi	Humic acids	3.19	
	Humup	Fulvic acids	1.70	
Organic matters	Humus	Humus Humines	0.42	
(%, w / w)		Total	5.33	
	Other organic compounds***		1.86	
		Total	7.19	
Vegetal material under	composed, % (w / w)	0.73		
Large-size fractio	Large-size fraction ****, % (w / w)		1.51	

*Related to the coarse soil sample; **Sulphates, phosphates, heavy minerals and relicts (from parental material); ***Organic compounds unbounded to humus; ****Granulometric fraction $\Phi > 2.00$ mm (including mineral fragments and non-altered parental rocks).

Major elements (%, w / w)			
SiO ₂	53.95		
Al ₂ O ₃	20.21		
Fe ₂ O ₃	2.85		
TiO ₂	0.06		
Na ₂ O	1.69		
K ₂ O	4.20		
MgO	1.26		
CaO	8.06		
P ₂ O ₅	0.37		
SO ₃	0.22		
CO ₂	4.83		
Σ	97.70		
Minor elements (μg /g)			
Cd	1.13		
Cr*	17.02		
Pb	78.05		
As	1.37		
Zn	93.74		
Cu	48.26		
Mn	217.85		

Table 3. Elemental chemical composition of soil samples

Table 4. Parameters estimated from linearization of the Freundlich and Langmuir isotherms,as well as from the linear isotherm for sorption of Acid Yellow 23 onto the soil

Isotherm	Equation	Estimated isotherm parameters		
Langmuir	V 150.04.1/0a + 0.540	R ²	q _m (mg g⁻¹)	K _L (L mg⁻¹)
	f = 150.24 1/6e + 0.549	0.9862	1.8218	0.00365
Freundlich Y	V 10105 los Co. 0.0004	R ²	n	K _F (mg L ^{1/n} /g mg ^{1/n})
	f = 1.0195 log Ce - 2.2384	0.9795	0.9807	0.3501
Linear	Y = 0.0069 Ce - 0.02	R ²	K _d (L Kg⁻¹)	-
		0.9811	6.94	-

by vineyards, in the same conditions of agricultural terracing $^{\mbox{\tiny 19}}.$

2. MATERIALS AND METHODS

2.1. Materials

Acid Yellow 23 (Tartrazine, CAS: 1934-21-0, Color index: 19140) provided by Sigma Aldrich was used without a previously purification.

The characteristics and composition of the investigated soil are presented in the Tables 1-4, where the pollution framing has been done concordant to literature ^{20,21}.

2.2. Methods

2.2.1. Soil samples preparation

The soil samples have been dried in a drying chamber for 3 h at a temperature of 105°C, and were further crushed in a Fritch agate mortar for 30 minutes at a rotative speed of 800 rev/min until a granulation ≤ 0.02 mm was reached. Representative samples were selected from the dried material for the microscopic studies. After removal of vegetal material, as well as of the large-sized material ($\emptyset > 2.00$ mm), the samples have been crushed up to a granulation ≤ 0.02 mm. The average samples (concordant to quarter method) for the physico-chemical analysis were obtained from the crushed material. The disintegration of the soil samples for the chemical analysis has been done by treatment with concentrated HCIO, and HNO, in two stages on sand bath, at the temperature of 400 - 450°C. SiO, from the primary minerals has been determined in the insoluble residue, while the other elements have been all determined in solution. pH was determined through potentiometry by the suspension procedure (10 g soil / 50 mL solution; granulation < 0,01 mm; contact time: 30 minutes), in bidistilled water with Cornning Pinnacle 555 multimeter and calomel-pH electrodes couple. The redox potential has been determined through the direct method with Pt- calomel electrodes couple.

2.2.2. Mineralogical analysis

The fractioning of raw soil samples and separation of the mineral fractions was performed throughout the isodynamic magnetic method and heavy-liquid methods (in bromoform) followed by concentration and purification of the mineral fraction by plane electrophoresis, solidliquid selective extraction and extraction in biphasic aqueous systems based on polyethylene glycol²². The mineralogical and chemical composition was assessed by: optical microscopy (MEYJ optic microscope), X-ray diffraction- DRX (diffractometer Phillips, CuKa radiation), IR spectrometry (Bio-Rad IR spectrometer, KBr pellet techique -matrix addition in blank method), Raman spectrometry (LabRAM INV-Horiba Jobin Yvon Raman spectrometer), thermal analysis (Netzsch TG 209 thermo-balance, Pt crucible, heating rate: 2.5°C/min), chemical analysis. The separation of the organic compounds has been carried-out by dichloroethane -methanol extraction (1-3 g soil; 1x25 mL, 3x15 mL), followed by GC-FID analysis (Hewlett-Packard 5972 chromatograph, silica column inactivated with n-hexane). The extracts were passed by the chromatographic column, being separated by successive elution four fractions: (1) elution with n-hexane (20 mL) - hydrocarbons and sulphur compounds (2) elution with n-hexane / toluene (4:1; 30 mL) - esters; (3) elution with n-hexane / ethyl acetate (35:2; 30 mL) - alkenonic compounds; (4) elution with n-hexane / ethyl acetate (4:1; 30 mL) - nalcohols, n-acids, steroid alcohol etc. The organic compounds from the first three fractions were determined by direct analysis, whereas those from the fourth fraction have been determined by derivatization with bis-(trimethylsilyl)-trifluoroacetamide in dichloroethane (0.5 mL reagent/ sample at 70°C, 2 h). For humus analysis, the free organic compounds have been removed from soil samples (1.0 - 1.5 g) by successive extraction with toluene, ethylic alcohol (95 %) and a mixture of toluene and ethylic alcohol 1:1 (10 mL/extraction). The separated solid phase has been refluxed with 50 mL solution HCl 2 %, for 1 h and after it was washed with methanol and dried at 50 °C. The remnant solid phase was separated by filtration, washed with methanol, dried at 50 °C and further extracted with a mixture of Na₂P₂O₇ 0.1 M and NaOH 0.1 M (pH=13). The humus from extract was determined by potentiometric titration²³.

SiO, was analyzed as follows: the silica from the parental material was determined by gravimetric analysis after solubilization of the other compounds, while the amorphous (pedogenetic) was analyzed by flame atomic absorption spectrometry in solution, with an AAS Vario 6 FL flame atomic absorption spectrometer (spectral buffer: CsCl1 % solution). Al, Na, K, Ca, Mg, Ti and have been determined by flame atomic absorption spectrometry after acid disaggregation without previous pre-concentration. The minor elements, (Cd, Cr, Pb, As, Ni, Zn, Mn, Co) were analyzed by flame atomic absorption spectrometry and UV-VIS molecular absorption spectrophotometry with an Rayleigh V-9200 spectrophotometer after pre-concentration through extraction. Sulphur was determined after complete mineralization to SO_4^{2-} and determination of the formed anion through potentiometry.

2.2.4. Sorption batch experiments

The experiments were performed by using a natural soil sampled from the depth of 0-15 cm in the industrial area of the city of lasi during the summer time (July 2008) that was previously dried and further screened to achieve soil particles size of above 2 mm, equilibration being carried-out with solution of CaCl₂. Experiments have been conducted in batch system at the room temperature. For the equilibrium study, 50 mL Acid Yellow 23 of different concentrations were mixed with a dose of 12 g L⁻¹ soil, the mixture being subjected to stirring at the room temperature as long it was needed to reach the equilibrium. The kinetic study was accomplished by using a concentration of 40 mg L⁻¹ and an amount of soil corresponding to a concentration of sorbent equal to 12 g L⁻¹. Specific amounts of sample have been withdrawn at certain time intervals, then filtered onto a 0.45 µm filter and finally analyzed to determine the concentration of dye by measuring the absorbance at λ_{max} = 427 nm with a CAMSPEC M-501 UV-VIS spectrophotometer. The percentage of dye removal (sorption efficiency) R % and the sorption capacity were calculated with the Eqs. (1)- (2):

$$R (\%) = \frac{C_i - C_e}{C_i} 100 \quad (1)$$

Table 5. Kinetic models applied for study of the Acid Yellow 23 sorption onto soil particles

Kinetic model	Equation	Parameters	
1st order equation	V - 2.0505v10-5+	R ²	0.588
$-\ln(C/C_0) = K_1 t$	1 = 3.0393×10 1	K ₁	3.059·10⁻⁵
2nd order equation	V 5 440×10-7 +	R ²	0.833
(1/C-1/C ₀)=K ₂ t	Y = 5.443×10 ° t	K ₂	5.442·10 ⁻⁷
pseudo 2nd order equations (type 1) $t/q=1/K_{_{21}}q_{_{e}}^{_{2}}-(1/q_{_{e}})t$		R ²	0.999
	Y = 3.727 t + 78.02	qe (exp)	0.265
		q _e	0.268
		K ₂₁	0.175
		R ²	0.935
pseudo 2nd order equations (type 2) $1/q=(1/K_{22}q_e^2)(1/t) + 1/q_e$	Y = 17.286 1/t + 4.46	q _e	0.224
		K ₂₂	1.153
pseudo 2nd order equations (type 3) q/t = $K_{23}qe^2 - (K_{23}q_e^2q)/q_e$	Y = 4.321 q + 0.23	R ²	0.860
		qe	-0.053
		K _{23qe}	-81.509

$$q (mg g^{-1}) = \frac{C_i - C_e}{m}$$
 (2)

where: Ci = initial dye concentration (mg L⁻¹), C_e = equilibrium concentration of dye in solution, m = sorbent dose (g L⁻¹).

All the experiments were carried-out at the natural pH of the solution (pH=7.5), pH measurements being performed with a Radelkis OP-271 pH-meter.

3. RESULTS AND DISCUSSIONS

3.1. The influence of contact time on the sorption of Acid yellow 23 by soil particles

In Fig. 1, the influence of the contact time upon the percentage removal (removal efficiency) and amount of Acid Yellow 23 sorbed onto the particles of soil of particle-size higher than 2 mm (sorption capacity) is presented

It may be observed that Acid Yellow 23 exhibits a sorption capacity of approximately 0.25 mg g⁻¹ and a reduced efficiency of the process, which is situated around 8 %. This fact may be explained by the strong electrostatic repulsion between the negatively charge of the soil and the sulphonic groups of the anionic dye. As it was observed, the main component of soil is SiO₂, an acidic oxide whose surface in aquatic solutions is negatively charged at pH > 2^{24} and even at pH below 2, silicon dioxide surfaces do not exhibit a strong tendency to acquire a positive charge²⁵. A very low adsorption of Acid Yellow 23 onto soil was also reported by other researchers ²⁶, where an average of 7.2 % (range 6-12.5) has been obtained for sorption of 5-60 mg L⁻¹ dye onto the investigated soil but sorption increased up to 44.9 % by mixing the soil with fly ash.





Fig.1. Influence of contact time on the removal efficiency (a) and sorption capacity (b) of Acid Yellow 23 onto the soil with particles higher than 2 mm



Fig. 2. Linearization of Langmuir (a), Freundlich (b) and linear (c) isotherms for sorption of Acid Yellow 23 onto soil with particles size above 2 mm

3.2. Sorption isotherms

The sorption isotherms are the equilibrium relationships between the concentration in the fluid phase and the concentration on the particles of sorbent at a given temperature. The fit of the experimental results through different isotherm models is an important method for finding the proper model for the design process as well as for improving the knowledge about the sorption mechanism. The most frequently used isotherms for describing the sorption process in the case of mono-component systems are the Langmuir, Freundlich and linear models. The Langmuir equation assumes that no interactions between the sorbate molecules exists, the sorption occurring in monolayer up to saturation and may be written in the linear shape in accordance to Eq. (3):

$$\frac{1}{q_{e}} = \frac{1}{q_{m}} + \frac{1}{K_{L}q_{m}} \frac{1}{C_{e}}$$
(3)

where: $q_e = \text{concentration of the solid phase in equilibrium}$ with the concentration of the liquid phase C_e , $q_m = \text{maxi-mum}$ sorbate uptake or maximum sorption capacity (mg g^{-1}) in the given conditions and K = Langmuir constant (L mg⁻¹).

The Freundlich equation involves the exponential distribution of the sorption sites resulting in a multilayer sorption and may be written with the Eq. (4):

$$\log q_e = \log K_F + \frac{1}{n_F} \log C_e \quad (4)$$

where K_{E} and 1/n are the Freundlich constants.

Equilibrium distribution of the sorbed compounds between solid (s) and water (w) sorption phase is characterized by a distribution (sorption) coefficient K_d defined by the Eq. (5):

$$K_{d} = \frac{C_{s}}{C_{w}} = \frac{q_{e}}{C_{e}} \quad (5)$$

where: $C_s = equilibrium$ sorbed concentration onto the solid (mg Kg⁻¹), $C_w = equilibrium$ liquid concentration (mg L⁻¹) and K_d (L Kg⁻¹) is the measure of interactions between the sorbate and the natural sorbent. Knowledge of K_d facilitates the assessment of the sorbate equilibrium concentration in a phase of a certain system if the one in the other phase is already known²⁷. K_d value is obtained from linear isotherm

$$q_e = K_d C_e \quad (6)$$

The parameters estimated from linearization of the Freundlich, Langmuir and linear (Fig. 2) isotherms for assessing the sorption of the studied dye onto the soil with particles size higher than 2 mm are presented in Table 4.

From the values of the correlation coefficient appears that the equilibrium data fitted best the Langmuir isotherm model, suggesting that the sorption of the studied compounds takes place in a monomolecular layer.

The content of organic carbon in the sorbent is in general, expressed as either the weight fraction of organic carbon f_{oc} or the weight fraction of organic matter f_{oM} . The amount of organic matter in typical mineral soils is usually ranged between 1 and 10 %, but is most of the time less than 5%. Since soil organic matter represents 58 % carbon (f_{oc} ~0.58 f_{oM}) the fraction of organic carbon is typically equal to 0.006-0.06 concordant to literature²⁸, in this case being equal to 0.0458.

Considering that:

$$K_{OC} = \frac{C_{OC}}{C_w} \quad (7)$$

where C_{oc} = concentration of the contaminant sorbed to organic matter, the relation between soil-partition coefficient K_a and organic carbon normalized sorption coefficient K_{oc} may be expressed in terms of Eq.(8):

which leads to a value of K_{oc} = 151.46 L Kg⁻¹. The very low value of K_{oc} shows that the dye tend to remain in solution indicating also its very high mobility, since it is considered that sorption coefficients less than 500 indicate a considerable potential for losses through leaching²⁹.

3.3. Sorption dynamics

The sorption kinetics have been studied by applying five kinetic models aiming at establishing the most suitable one for describing the sorption of the investigated azo dye onto the particles of investigated soil. The model equations used for fitting the kinetic data are:

- 1st order equation;
- 2nd oder equation;
- pseudo 2nd order equations of types 1, 2 and 3.

The kinetic parameters resulted by the kinetic study are presented in Table 5. The results reveal that the sorption of Acid Yellow 23 onto particles of soils follows a pseudo second order kinetics, suggesting that the chemisorption is the rate controlling mechanism. Among the three types of pseudo second order models applied, the type 1 proved to be the most adequate, not only from the point of view of the correlation coefficient but also due to the fact that the calculated values of the sorption capacities have been in very good agreement with the experimental ones. However, the values of constants K and sorption capacities q obtained from the three linear shapes of the pseudo second order models were different. The values of q of the types 2 and 3 of the pseudo-second order model resulted to be lower than their experimental equivalents. The last model produced negative values of the constant K₂₃ which is experimentally and practically impossible. A similar behavior was reported for sorption of Acid Yellow 23 (tartrazine) on anion exchange resin as Amberlite³⁰.

4. CONCLUSIONS

The capacity of the soil sampled from the lasi area (city situated in the north-eastern part of Romania) to retain the basic dye Acid Yellow 23 from aqueous solution by sorption has been studied in this paper. The soil has been mineralogically and chemically characterized. The sorption equilibrium revealed that the soil with particles higher than 2 mm may uptake 0.25 mg g⁻¹. The reduced percent of sorption may be explained by the strong electrostatic repulsion between the negative charge of the soil, whose main component is silica, and the sulphonic groups of the anionic dye. The sorption process is best represented by the Langmuir isotherm indicating a monolayer sorption, the sorption sites being equivalent from the energetic point of view. A pseudo-second order kinetic model can be efficiently used to predict the kinetic of sorption of Acid Yellow 23 onto the investigated soil. The low value of the organic carbon normalized sorption coefficient $K_{\rm oc}$ suggests a high potential of leaching that could result in contamination of the groundwater.

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BIBLIOGRAPHY

- MacCara M.E. Tartrazine: a potentially hazardous dye in Canadian drugs. CMA Journal, 126, 910–914, 1982
- 2. Jain R, Bhargava M, Sharma N. Electrochemical Studies on a Pharmaceutical Azo Dye: Tartrazine. Ind Eng Chem Res 42, 243–247, 2003
- 3. Smolinske S.C. Handbook of food, drug, and cosmetic excipients. CRC Press, 1992
- 4. Otterstätter G. Coloring of Food, Drugs and Cosmetics. Marcel Dekker Inc, NY, 1999
- SCCNFP/0786/04 Opinion of the scientific committee on cosmetic products and non-food products intended for consumers concerning Acid Yellow 23, on line at: http://ec.europa.eu/health/ph_risk/committees/sccp/documents/out260_en.pdf
- 6. Holistic Health Encyclopedia, on line at: http://www. findhealer.com/glossary/T.php3
- Rowe K.S., Rowe K.J. Synthetic food coloring and behavior: a dose response effect in a double-blind, placebo-controlled, repeated-measures study. J Pediatr 25, 691-698, 1994
- 8. Desphande S.S. Handbook of Food Toxicology, CRC Press, 2002
- Chisvert A, Chafer A, Salvador A Colouring agents in decorative and other cosmetics. Analytical Methods. In: Salvador A, Chisvert A. (ed) Analaysis of cosmetic products. Elsevier, 141-211, 2007
- Caliman F.A., Apostol L.C., Hlihor R.M., Gavrilescu M. Factors influencing the sorption of anionic azo dye tartrazine from aqueous solutions onto natural clay, Materiale si procese inovative, 455-460, 2008
- Qiao S., Hu Q, Haghseresht F., Hu X., Lu G.Q. An investigation on the adsorption of acid dyes on bentonite based composite adsorbent. Sep Purif Technol 67, 218-225, 2009
- Mittal A., Mittal J., Kurup L. Adsorption isotherms, kinetics and column oprations for the removal of hazardous dye Tartrazine from aqueous solutions using waste materials-Bottom Ash and De-Oiled Soya as asdorbents. J Hazard Mater 136, 567-578, 2006
- Mittal A, Kurup L, Mittal J Freundlich and Langmuir adsorption isotherms and kinetics for the removal of Tartrazine from aqueous solutions using hen feathers. J Hazard Mater 146, 243-248, 2007
- Behnajady M.A., Modirshahla N., Hamzavi R. Kinetic study on photocatalytic degradation of C.I. Acid Yellow 23 by ZnO photocatalyst. J Hazard Mater 133, 226-232, 2006
- Daneshvar N., Khataee A.R., Amani Ghadim A.R., Rasoulifard M.H. Decolorization of C.I. Acid Yellow 23 solution by electrocoagulation process: Investigation of operational parameters and evaluation of specific electrical energy consumption (SEEC). J Hazard Mater 148, 566-572, 2007
- Hashi H.A.A., Mohamed A.R., Teong L.K. Solar photocatalytic degradation of tartrazine using titanium dioxide. Jurnal Teknologi 35, 31-40, 2001
- Rao K.V.S., Lavedrine B., Boule P. Influence of metallic species on TiO2 for the photocatalytic degradation of dyes and dye intermediates. J Photochem Photobiol A: Chem, 154,189-193, 2003
- Modirshahla N., Behnajady M.A., Ghanbary F. Decolorization and mineralization of C.I. Acid Yellow 23 by

Fenton and photo-Fenton processes. Dyes Pigments, 73, 305-310, 2007

- Iancu O.G., Buzqar N. The geochemical atlas of heavy metals in the soils of the municipality of lasi and its surrounding areas. Al.I Cuza University Publishing House, Iasi, 2009
- 20. Adriano D.C. Trace elements in terrestrial environments: biogeochemistry, bioavailability, and risks of metals, 2nd edition. Springer, New York 2001
- 21. Kabata-Pendias A., Mukherjee A.B. Trace Elements from Soil to Human. Springer, Berlin Heidelberg, 2007
- 22. Bulgariu L., Bulgariu D. Extraction of metal ions in aqueous polyethylene glycol-inorganic salt twophase systems in the presence of inorganic extractants: Correlation between extraction behaviour and stability constants of extracted species. J Chromatog A 1196-1197, 117-124, 2008
- Bulgariu D., Jurvale D., Bulgariu L., Macoveanu M., Rusu C. Distribution and migration of chrome in urban soils-case study: lasi city (industrial zone). Environmental Engineering and Management Journal, 7, 277-288, 2008
- 24. Judd S. Process science and engineering for water and wastewater treatment. IWA Publishing, 2002
- 25. Donovan R.P. Contamination-free manufacturing for semiconductors and other precision products. CRC Press, 2001
- Albanis T.A., Hela D.G., Sakellarides T.M., Danis T.G. Removal of dyes from aqueous solutions by adsorption on mixtures of fly ash and soil in batch and column techniques. Global Nest the International Journal, 2, 237-244, 2000
- Toul J., Bezdek J., Kovarova M., Bohacek Z., Hanak J., Milicka J., Muller P. Sorption of hydrophobic organic pollutants on soils and sediments. Bulletin of Geoscience 78, 205-223, 2003
- 28. Weiner E.R. Applications of environmental aquatic chemistry: a practical guide. CRC Press, 2008
- 29. Gavrilescu M. Fate of pesticides in the environment and its bioremediation. Eng Life Sci 5, 497-526, 2005
- Wawrzkiewicz M., Hubicki Z. Removal of tartrazine from aqueous solutions by strongly basic polystyrene anion exchange resins. J Hazard Mater 164, 502-509, 2009