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Sorption of chrysoidine by row cork and cork entrapped in calcium alginate beads

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Abstract Azo-dyes, molecules characterised by the presence of the azo-group (–N═N–), are widely used in textile, leather, rubber, plastic, and food industries. Water-soluble azo-dyes are greatly resistant to biodegradation, and are characterised by a high thermal and photo stability due to their complex structures. The release of these molecules into the environment is of crucial concern due to their toxic, mutagenic and carcinogenic characteristics. Biosorption has been demonstrated an effective method to remove pollutants from wastewaters thus solving ecological tasks, being a low cost process and the sorbent biodegradable. The main requirements of an efficient sorbent are thermal, chemical and mechanical stability, and rapid sorption.

In this work, the ability of both row cork and the same sorbent entrapped in a biopolymeric gel of calcium alginate, on the removal of chrysoidine from aqueous solutions was examined.

The influence on the sorption of pH, initial dye concentration, and particle size, as well as the efficiency of the entrapment, have been investigated. The maximum sorption was found for cork samples of fine particle size (FC), in both row and entrapped forms, at pH 7; conversely, at pH 4 the difference is significant (0.12 mmol/g for row cork and 0.20 mmol/g for entrapped cork), evoking a cooperation of alginate in binding the positively charged chrysoidine molecule.

1. Introduction

Among the various techniques for removal of pollutants from waste waters (chemical precipitation and filtration, biodegradation, electro-chemical treatments, chemical coagulation, reverse osmosis, ion exchange, oxidation and adsorption), sorption of both metal ions and organic molecules from waters by biomass has been found to be an effective removal method, due to its efficiency, simplicity, easy applicability, and

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cost-effectiveness (Guiso et al., 2012; Nurchi and Villaescusa, 2012). Cork, thanks to the different chelating groups on its surface, behaves as a strong sorbent towards most of the polluting metal ions (Villaescusa et al., 2002) and it presents good perspectives for organic contaminants (Nurchi et al., 2010, 2008; Nurchi and Villaescusa, 2008).

Azo-dyes, molecules characterised by the presence of the azo-group (–N═N–), are widely used in the textile, leather, rubber, plastic, and food industries (Erkurt, 2010). Water-soluble azo-dyes are greatly resistant to biodegradation, and are characterised by a high thermal and photo stability due to their complex structures. Large volumes of coloured effluents are discharged into receiving waters: the coloured wastewater may to some extent inhibit vital photosynthetic processes, and, furthermore, produces an unpleasant environmental impact. The release of these molecules into the environment is of crucial concern due to their toxic, mutagenic and carcinogenic characteristics. Toxic effluents containing azo-dyes are discharged from various industries and they pose toxicity (genotoxicity, mutagenicity, carcinogenicity with often lethal effects) to aquatic organisms (bacteria, algae, fish, . . .) and animals (Puvaneswari et al., 2006). Thus, the removal of azo-dyes from wastewaters is a fundamental environmental issue.

Chrysoidine is a synthetic azo-dye widely used in the textile industry. It undergoes reduction followed by a chain of reactions leading to the formation of toxic compounds. Oral administration of chrysoidine results in liver-cell adenomas, carcinomas and leukaemia in animals, and some case studies suggest its carcinogenicity as well (Lei et al., 2011). Various researchers have studied the adsorption of this dye on different materials. Activated carbon has been found to be effective, having both high surface area and high sorption capacity. However, its relatively high operation costs hamper its large-scale application. Therefore, a number of low-cost sorbents have been examined for dye removal (Ho and McKay, 1998; Matheswaran and Karunanithi, 2007; Mittal et al., 2010; Purkait et al., 2004). It is also recognised that, in order to facilitate sorbent application, the raw material can be entrapped in calcium alginate gel matrix. Alginates are salts of unbranched copolymers of β-D-mannuronic and α-L-guluronic acids extracted mainly from brown seaweed. By association with most divalent cations, such as calcium, they produce thermally irreversible gels. Calcium alginate was used as an encapsulating polymeric matrix due to its low-cost, biodegradability, high and easy encapsulation capability. This kind of encapsulating procedure was successfully applied for the entrapment of grape stalk waste from wine production and solid by-products from electroplating and metal surface treatment industries (Garlaschelli et al., 2013).

In the present work, cork has been investigated as sorbent for Chrysoidine G (Fig. 1).

The comparison among the maximum sorption capacity of row cork samples at two different particle sizes (labelled as FC and GC with nominal diameter over 40 mesh and between 20–40 mesh, respectively) and the finest cork fraction (FC) entrapped in calcium alginate gel beads has been examined at 25 °C and at two different pH. In particular pH 4 and 7 are chosen to study the effect of the surface charge of the solid phase on the dye sorption.

A spectrophotometric study of the protonation properties of Chrysoidine G is furthermore presented to elucidate the sorption mechanism of the dye on the biosorbent.

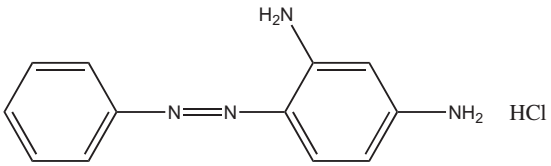

Figure 1 Chemical structure of Chrysoidine G.

2. Experimental

2.1. Materials

All the reagents (Chrysoidine G, calcium alginate, $CaCl_2$, KOH, KCl and HCl), purchased from Aldrich (analytical grade), were used without further purification. Chrysoidine G (1,3-benzenediamine, 4-(phenylazo)-monohydrochloride M.W. 248.72) is highly soluble in water. A stock solution of Chrysoidine G was prepared by dissolving the proper amount in double distilled water. Cork was kindly supplied by cork taps manufacturer from Cassà de la Selva, Girona (Spain). Cork samples of two different sizes were selected according to the Tyler mesh size (Particle Size – US Sieve Series and Tyler Mesh Size Equivalents, 2009) and labelled as FC and GC (nominal diameter over 40 Mesh and between 20–40 Mesh, respectively). Cork particles, rinsed three times with boiling water and three times with distilled water, were dried in a vacuum oven at 60 °C, then stored in a desiccator at room temperature. Alginate beads containing 2% (w/v) FC particles entrapped into a calcium alginate gel were obtained, following the procedure previously reported by Fiol et al. (2004, 2005). Sodium alginate salt was used as the gelling material, with 0.1 M $CaCl_2$ as fixing solution.

2.2. Chrysoidine G chemical characterisation

Protonation equilibrium of Chrysoidine G was studied by spectrophotometric titration. The experiments were performed in a thermostated glass cell equipped with a magnetic stirrer, a glass electrode (Metrohm LL UNITRODE), connected to a pH-metre (Metrohm 691), an inlet–outlet tube for Argon and a fibre optic dip probe connected to a Varian Cary 50 UV–vis spectrophotometer. The accuracy and precision of this equipment were previously determined by Crisponi et al. (2004). The potentiometric cell was standardised in the H^+ concentration employing alkalinimetric titrations of HCl with KOH, at ionic strength 0.1 M KCl, and the results were analysed with Gran procedure (Gran, 1952). The protonation equilibrium has been studied on 15 solutions of 0.1 M KCl, at different pH (ranging from 3 to 8) containing Chrysoidine G 5.6×10^{-5} M. The pH of each solution was adjusted by adding small amounts of HCl 0.01 M or KOH 0.01 M and it is measured with the above described calibrated cell. The spectrum of each solution was recorded in the 300–600 nm spectral range with 1 cm path length and the data were processed by Hyperquad program (Gans et al., 1996).

2.3. Sorption isotherm procedure

Sorption isotherms are widely used to characterise retention of chemicals in solid phase. In our experiments, a fixed amount

(0.5 g) of dry row cork samples (FC or GC) or alginate encapsulated FC (in an amount corresponding to 0.5 g of dry FC) was contacted with 40 mL of solutions at equal pH, but at different Chrysoidine G content, in a series of Falcon™ 50 mL tubes. The suspensions were stirred overnight on a Falc F200 tube rotator operating at constant speed of 9 rpm. After equilibration, the suspensions were filtered through Whatman filter paper, Grade 4, 20–25 μm. The filtrate was analysed by a Varian Cary 50 UV–vis spectrophotometer measuring the absorbance at 410 nm to determine the equilibrium dye concentration in the solution phase. The content of dye sorbed, per unitary weight of solid phase in each experiment, Q_i (mmol g^{-1}), has been evaluated from the difference between initial, $C_{i,i}$ (mol dm^{-3}), and equilibrium $C_{e,i}$ (mol dm^{-3}) dye concentrations in solution:

$$Q_i = \frac{(C_{i,i} - C_{e,i})}{(\text{mass of dry sorbent})} \times V_S \quad (1)$$

where V_S is the solution volume in mL, and the mass of dry sorbent in grams.

2.4. Kinetics studies

In order to assess the time needed to reach equilibrium, four sets (two for FC and two for FC alginate beads, at pH 4 and 7) of 12 tubes were prepared. A fixed quantity of solid material (0.5 g) was contacted with a solution (V_S = 40 mL) of fixed Chrysoidine G concentration following the sorption procedure above described. The solution phases were analysed after different contact times to determine the kinetics profiles by plotting the Q value vs. the contact time, t.

3. Results and discussion

3.1. Chrysoidine G chemical characterisation

The protonation equilibrium of Chrysoidine G was studied by spectrophotometric titration. Actually, the low solubility of this dye prevents the determination of its protonation constant by means of a simple potentiometric titration. Furthermore the knowledge of the spectral variations with pH has been useful in the analytical determination of free dye after the sorption processes. The spectra of the examined solutions at constant Chrysoidine G concentration and variable pH are registered and reported in Fig. 2. A maximum, due to the protonated species LH^+, is evident at 454 nm, characterised by a molar absorptivity of 26 500 M^{-1} cm^{-1}. By increasing the pH, the intensity of this band decreases and a new composite band of the deprotonated species, L, appears at 397 nm with an absorptivity value of 13 400 M^{-1} cm^{-1}. A sharp isosbestic point is clearly observed at 410 nm.

In order to obtain the protonation constant of Chrysoidine G, the absorbance values have been processed by the program Hyperquad (Gans et al., 1996). A log K value of 5.41(2) has been obtained, and the resulting speciation plot is shown in Fig. 3.

The diagram of Fig. 3 can be helpful in the selection of an effective solid sorbent for the removal of the dye. Indeed, in solutions at pH lower than 5, the positively charged protonated species (LH^+) is the prevalent form of Chrysoidine G. Hence, in acidic media, the dye can be efficiently sorbed onto a negatively charged solid material. On the contrary, at pH higher than 6 the neutral species L of Chrysoidine G is predominant, so that the surface charge of the sorbent could be irrelevant since the main sorption mechanism is not an ion exchange.

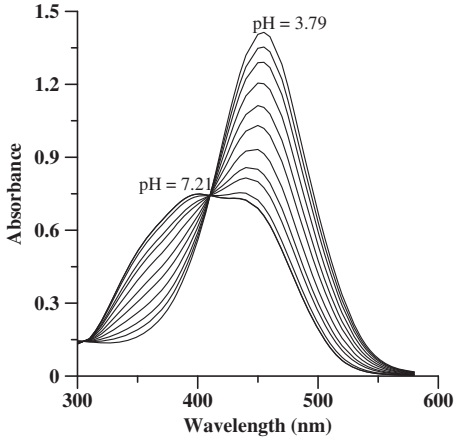

Figure 2 Spectra of chrysoidine 5.6×10^{-5} M, path length 1 cm, and variable pH from 3.79 to 7.21.

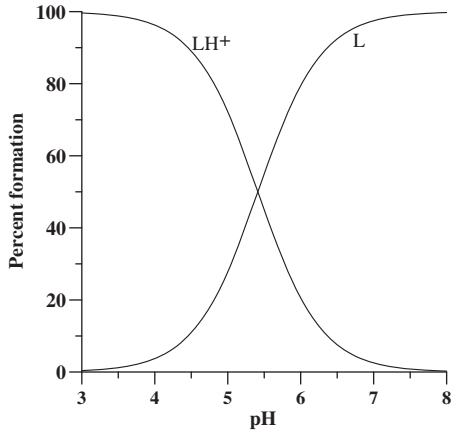

Figure 3 Speciation plot of Chrysoidine G.

3.2. Effect of pH on dye sorption

Just as pointed out in the previous Section 3.1, one of the most important parameters to take into account in the sorption process is the pH of the solutions that must be treated with the sorbents. Actually, the pH may influence the chemical speciation of the dye as well as the charge of the sorbent surface. It has been demonstrated, by potentiometric titrations, that row cork surface is positively charged in acidic solution, indeed the point zeta charge (PZC) of this biosorbent is reported to be 3.6 ± 0.1 (Villaescusa et al., 2002). Since, the pK_a values for the components of alginate structure, guluronic and mannuronic acids, have been reported to be 3.65 and 3.38, respectively (Percival and McDowell, 1967) and assuming the same constants for the alginate gel, the surface of the beads of cork entrapped in calcium alginate gel is uncharged at pH lower than 2, whereas it is negatively charged at pH higher than 5 (Fig. 4).

For all these reasons we choose to perform all sorption experiments at pH 4 and at pH 7 with the aim to detect possible differences in the Chrysoidine G sorption on row cork and on cork entrapped in calcium alginate beads. Indeed at pH 4 the row cork surface is almost uncharged (being the PZC around 3.6) but the alginate still retains only ~25% of uncharged surface, and, at this pH Chrysoidine G is mainly present in its protonated LH^+ form (see the speciation plot in Fig. 3), an higher maximum sorption capacity should be expected for the cork entrapped in calcium alginate beads. At pH 7, the surface of both row cork and cork entrapped in calcium alginate beads is totally negatively charged and the dye is mainly present as deprotonated neutral species, so a similar sorption behaviour can be presumable.

3.3. Sorption kinetics

As a preliminary step, kinetics sorption experiment at pH 4 and 7, for both FC and the same material entrapped in calcium alginate gel were carried out, following the experimental procedure described in Section 2.3. The resulting kinetic profiles are reported in Fig. 5.

Various sorption kinetic mechanistic models have been used to describe the uptake of analytes on solid sorbents, but when dealing with biomaterial, it is often difficult to describe the whole kinetics data range, and important deviations from predicted models are observed (Lodeiro et al., 2006). This is the reason why empirical expressions are commonly preferred, and pseudo first-order and pseudo second-order equations, are the most widely used (Alberti et al., 2012).

The kinetic profiles of Fig. 5 reveal that the time needed to achieve equilibrium is around 3 h in all the four cases. On the other hand, different behaviours can be observed between cork (a) and the entrapped cork (b), while no differences due to the pH are evident. In Fig. 5 pseudo second-order fitting curves are also shown, being the best fitting.

3.4. Sorption isotherms

The sorption isotherms have been evaluated in five conditions, considering the same four sets as above described for the kinetic studies, and adding a further one set obtained by equilibration of the solution with GC with a nominal diameter of 20 mesh at pH 7. For operative reasons, all suspensions were left stirring overnight (equilibration time much longer than that required on the basis of kinetic results).

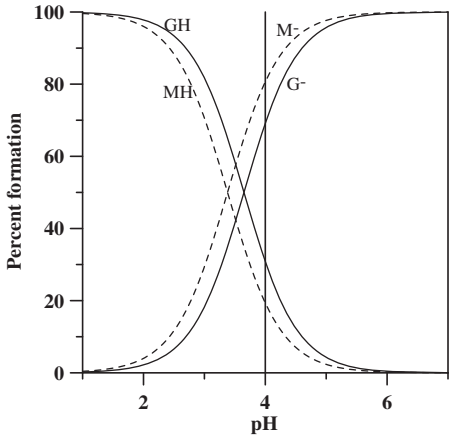

Figure 4 Speciation plots of mannuronic (MH) and guluronic (GH) acids, the main components of alginate gel.

The experimental results, reported in Fig. 6 for row cork (FC and GC) and entrapped FC at the two different pH's, can be modelled by the simplest Langmuir equation:

$$Q = \frac{Q_{max} \times K \times C}{1 + K \times C} \quad (2)$$

where Q (mmol g^{-1}) is the amount of sorbate at equilibrium, Q_{max} (mmol g^{-1}) the monolayer saturation capacity at a given pH, K (M^{-1}) the Langmuir constant and C (mol L^{-1}) is the analyte concentration at equilibrium in the solution phase.

From the maximum sorption capacity obtained by the Langmuir fitting it is possible to estimate the specific surface area (S) that can be calculated by the following equation (Itodo et al., 2010; Kaewprasit et al., 1998):

$$S = Q_{max} \times a \times N_A \times 10^{-20} \quad (3)$$

where S is the specific surface area in 10^{-3} km^2 kg^{-1}; Q_{max} (mmol g^{-1}) the maximum sorption capacity, a is the occupied surface area of one molecule of Chrisoidyne G = 31.2 Å (http://www.chemspider.com/Chemical-Structure.10316.html); N_A is the Avogadro's number, 6.02×10^{23} mol^{-1}.

The parameters K and Q_{max}, evaluated by a non-linear least squares procedure, and the computed specific area surface, S, are reported in Table 1. A pretty good fitting is obtained in all the five cases.

3.5. Discussion

The FC material is able to sorb Chrysoidine G about 30% more than GC, as expected on the basis of the larger surface of the former. No significant differences are observed for the intensive parameter K relative to the strength of interaction. The maximum sorption capacity, expressed as mmol g^{-1}, of Chrysoidine G sorbed by FC at pH 7 is more than twice of that sorbed at pH 4. The lower sorption at pH 4 can be rationalised taking into account the repulsive action exerted by the row cork surface towards Chrysoidine G, both being positively charged at this pH. Furthermore, the lower K value calculated at pH 4 (8.1 *vs* 10.0) supports this repulsive effect.

The Q_{max} values strictly resemble those found for cork with copper (Q_{max} 0.33 mmol g^{-1}) and nickel (Q_{max} 0.18 mmol g^{-1}), thus indicating that, even with completely different sorbates (azo-molecule or metal ions), the surface binding sites are similar in number and, perhaps, in chemical form (Nurchi et al., 2008).

What are the effects of entrapping cork in alginate beads? First of all it is important to point out that the amount of Chrysoidine G sorbed onto alginate beads prepared without cork (blank) is negligible (about one order of magnitude lower) compared to the Q_{max} obtained for row cork and cork entrapped in calcium alginate beads for both the pH values considered here. It is clear that the calcium alginate coating interferes both with the kinetic and with the thermodynamic behaviour. A qualitative evaluation of kinetic curves in Fig. 5 shows that the time needed by beads to reach equilibrium at pH 7 is about 1.5 times greater than that of row cork, being almost similar at pH 4. The increase in equilibration time

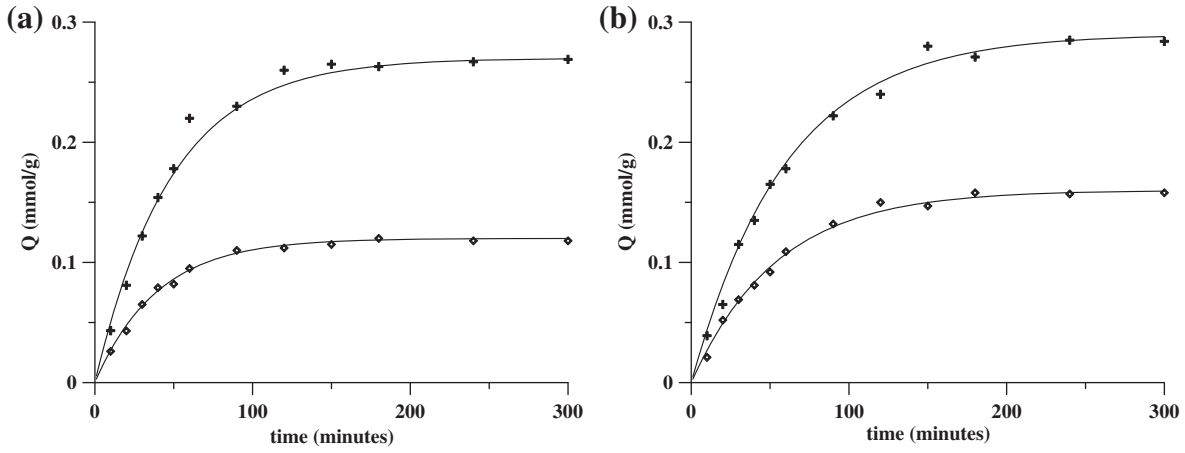

Figure 5 Kinetic behaviour of FC row cork (a) and FC cork entrapped in alginate beads (b). Symbol + refers to pH 7, and ◇ to pH 4.

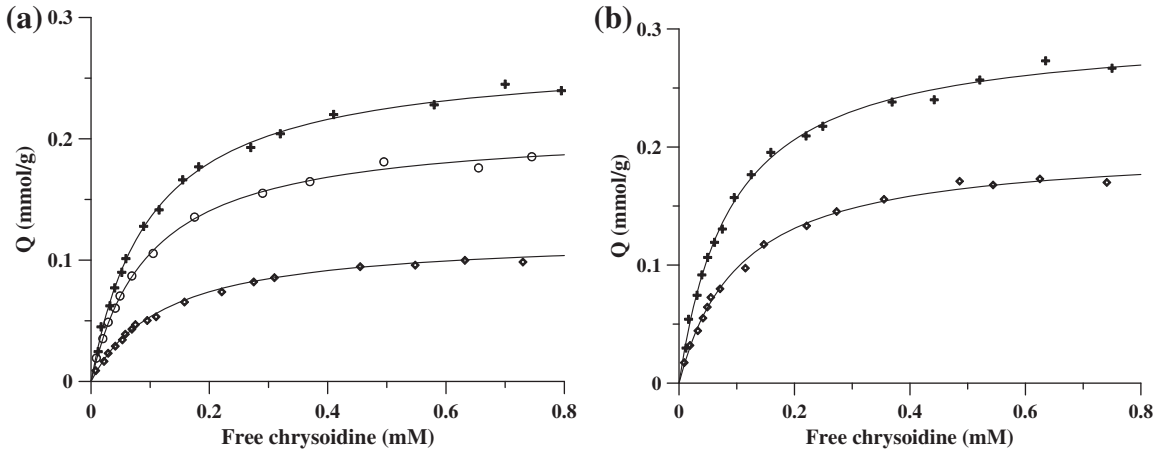

Figure 6 Content of sorbed dye per unitary weight of sorbent, Q, is reported as a function of free chrysoidine at equilibrium. (a) FC at pH 7 (+), GC at pH 7 (o), and FC at pH 4 (◇); (b) cork in alginate beads at pH 7 (+) and at pH 4 (◇).

Table 1 Langmuir parameters, and the specific area surface calculated for the Chrysoidine G sorption on row cork (FC and GC) and FC encapsulated in alginate beads.

pH	Case	K (m M^{-1})	Q_{max} (mmol g^{-1})	Q_{max} (mg/g)	SSR^*	S (10^{-3} km^2 kg^{-1})
4	FC	8.1(1)	0.12(2)	36.3	0.61×10^{-4}	22.54
	Beads	9.5(2)	0.20(2)	42.4	1.63×10^{-4}	37.56
7	FC	10.0(1)	0.27(1)	57.3	2.00×10^{-4}	50.71
	GC	10.1(2)	0.21(2)	44.6	0.96×10^{-4}	39.44
	Beads	11.1(1)	0.29(3)	61.5	2.41×10^{-4}	54.47

* *SSR* is the sum of the square residuals.

at pH 7 should depend on a limiting step in Chrysoidine G reaching cork through the external alginate: no attraction is exerted by the negatively charged surface of alginate towards the neutral form of Chrysoidine G at this pH. On the contrary, at pH 4 the partially negatively charged alginate surface attracts the positively charged protonated species of Chrysoidine G. As far as the thermodynamic point of view, while at pH 7 the Q_{max} for cork and cork entrapped is almost the same in the limits of experimental errors, at pH 4 the difference is highly significant (0.12 for FC and 0.20 for entrapped FC), evoking a positive contribution of alginate in binding the positively charged Chrysoidine G molecule.

4. Conclusions

The presented results on Chrysoidine G sorption by a biomass easily available in the Mediterranean area suggest that this material, mainly studied for metal sorption, can find interesting environmental applications devoted to the treatment of industrial wastewater streams contaminated by dyes or by

similar organic pollutants. The entity of removed dye per gram of biomass, is extremely encouraging, and also the coating of cork with calcium alginate produces favourable contribution in particular at those pH values at which cork alone is less effective.

It is also interesting to highlight that the maximum sorption capacity here obtained by using cork as biomass for Chrysoidine G is of the same magnitude order, or sometimes higher, compared to the values obtained by other natural sorbents for azo-dyes, as for example peanut husk (Sadaf and Bhatti, 2013), sugarcane bagasse (Zhang et al., 2011) or pine cone (Dawood and Sen, 2012).

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References

Alberti, G., Amendola, V., Pesavento, M., Biesuz, R., 2012. Beyond the synthesis of novel solid phases: review on modelling of sorption phenomena. Coord. Chem. Rev. 256 (1–2), 28–45.

Crisponi, G., Caredda, A., Cristiani, F., Diaz, A., Nurchi, V.M., Pinna, R., Pivetta, T., Silvagni, R., 2004. Evaluation of a fibre optic device in solution equilibria studies. Application to 3-hydroxybenzoic acid ionization. Anal. Chim. 94 (3), 147–153.

Dawood, S., Sen, T.K., 2012. Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: equilibrium, thermodynamic, kinetics, mechanism and process design. Water Res. 46 (6), 1933–1946.

Erkurt, H.A., 2010. Biodegradation of Azo Dyes, vol. 9. Springer-Verlag, Berlin Heidelberg.

Fiol, N., Poch, J., Villaescusa, I., 2004. Chromium (VI) uptake by grape stalks wastes encapsulated in calcium alginate beads: equilibrium and kinetics studies. Chem. Speciation Bioavailability 16, 25–33 (1–2 SPEC. ISS.).

Fiol, N., Poch, J., Villaescusa, I., 2005. Grape stalks wastes encapsulated in calcium alginate beads for Cr(VI) removal from aqueous solutions. Sep. Sci. Technol. 40 (5), 1013–1028.

Gans, P., Sabatini, A., Vacca, A., 1996. Investigation of equilibria in solution. determination of equilibrium constants with the HYPERQUAD suite of programs. Talanta 43 (10), 1739–1753.

Garlaschelli, F., Alberti, G., Fiol, N., Villaescusa, I., 2013. Application of anodic stripping voltammetry to assess sorption performance of an industrial waste entrapped in alginate beads to remove As(V). Arabian J. Chem. (http://dx.doi.org/10.1016/j.arabc.2013.01.003).

Gran, G., 1952. Determination of the equivalence point in potentiometric titrations. Part II. Analyst 77 (920), 661–671.

Guiso, M.G., Alberti, G., Emma, G., Pesavento, M., Biesuz, R., 2012. Pb(II), Cu(II) and Cd(II) removal through untreated rice husk; thermodynamics and kinetics. Anal. Sci. 28 (10), 993–999.

Ho, Y.S., McKay, G., 1998. The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat. Can. J. Chem. Eng. 76 (4), 822–827.

Itodo, A.U., Itodo, H.U., Gafar, M.K., 2010. Estimation of specific surface area using Langmuir isotherm method. J. Appl. Sci. Environ. Manage. 14 (4), 141–145.

Kaewprasit, C., Hequet, E., Abidi, N., Gourlot, J.P., 1998. Application of methylene blue adsorption to cotton fiber specific surface area measurement: part I. Methodology. J. Cotton Sci. 2 (4), 164–173.

Lei, H., Liu, J., Song, L., Shen, Y., Haughey, S.A., Guo, H., Yang, J., Xu, Z., Jiang, Y., Sun, Y., 2011. Development of a highly sensitive and specific immunoassay for determining chrysoidine, a banned dye, in soybean milk film. Molecules 16 (8), 7043–7057.

Lodeiro, P., Herrero, R., Sastre De Vicente, M.E., 2006. Thermodynamic and kinetic aspects on the biosorption of cadmium by low cost materials: a review. Environ. Chem. 3 (6), 400–418.

Matheswaran, M., Karunanithi, T., 2007. Adsorption of Chrysoidine R by using fly ash in batch process. J. Hazard. Mater. 145 (1–2), 154–161.

Mittal, A., Mittal, J., Malviya, A., Gupta, V.K., 2010. Removal and recovery of Chrysoidine Y from aqueous solutions by waste materials. J. Colloid Interface Sci. 344 (2), 497–507.

Nurchi, V.M., Villaescusa, I., 2008. Agricultural biomasses as sorbents of some trace metals. Coord. Chem. Rev. 252 (10–11), 1178–1188.

Nurchi, V.M., Villaescusa, I., 2012. Sorption of toxic metal ions by solid sorbents: a predictive speciation approach based on complex formation constants in aqueous solution. Coord. Chem. Rev. 256 (1–2), 212–221.

Nurchi, V.M., Pinna, R., Fiol, N., Villaescusa, I., 2008. Use of cyclic voltammetry to evaluate sorption properties of cork residues towards Mn(II) in waters. J. Solution Chem. 37 (4), 477–485.

Nurchi, V.M., Crisponi, G., Villaescusa, I., 2010. Chemical equilibria in wastewaters during toxic metal ion removal by agricultural biomass. Coord. Chem. Rev. 254 (17–18), 2181–2192.

Particle Size – US Sieve Series and Tyler Mesh Size Equivalents; Tyler Screening Company, 2009.

Percival, E., McDowell, R.H., 1967. Chemistry and Enzymology of Marine Algal Polysaccharides. Academic Press, London and New York.

Purkait, M.K., Gusain, D.S., DasGupta, S., De, S., 2004. Adsorption behavior of chrysoidine dye on activated charcoal and its regeneration characteristics by using different surfactants. Sep. Sci. Technol. 39 (10), 2419–2440.

Puvaneswari, N., Muthukrishnan, J., Gunasekaran, P., 2006. Toxicity assessment and microbial degradation of azo dyes. Indian J. Exp. Biol. 44 (8), 618–626.

Sadaf, S., Bhatti, H.N., 2013. Evaluation of peanut husk as a novel, low cost biosorbent for the removal of Indosol Orange RSN dye from aqueous solutions: batch and fixed bed studies. Clean Technol. Environ. Policy, http://dx.doi.org/10.1007/s 10098-013-0653-z.

Villaescusa, I., Fiol, N., Cristiani, F., Floris, C., Lai, S., Nurchi, V.M., 2002. Copper(II) and nickel(II) uptake from aqueous solutions by cork wastes: a NMR and potentiometric study. Polyhedron 21 (14–15), 1363–1367.

Zhang, Z., Moghaddam, L., O'Hara, I.M., Doherty, W.O.S., 2011. Congo red adsorption by ball-milled sugarcane bagasse. Chem. Eng. J. 178, 122–128.