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Elimination of organic water pollutants using adsorbents obtained from sewage sludge*

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Abstract

Sewage sludge valorisation must be the preferred management solution for a residue which minimising does not keep with a desirable improvement on wastewater treatment. This research work deals with the potential application of adsorbents produced from sewage sludge in organic pollutants removal. After chemical activation and pyrolysis treatment, sewage sludge provides materials of great porosity and high surface area. The properties of this type of material was studied by liquid-phase adsorption using crystal violet, indigo carmine and phenol as adsorbates, experiments being performed for two different adsorbent particle sizes. Firstly, single adsorption batch experiments were carried out to obtain kinetic and equilibrium data. The adsorbate's preferential adsorption was then investigated by studying adsorption from mixed solutions. The sludge-derived activated carbon produced could adsorb the three adsorbates considered with the time required to reach equilibrium and full adsorptive capacity varying between the adsorbates. Crystal violet adsorption has been higher and faster than indigo carmine or phenol. It is proposed that activated carbons made from sewage sludge show promise for the removal of organic pollutants from aqueous streams.

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1. Introduction

Sewage sludges are by-products derived from the regular activities of wastewater treatment plants. It is estimated that an average production of 40–60 g dry matter/inhabitant/day is typical for urban sewage plants [1], to which must be added a

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corresponding amount produced by industrial sewage plants. Production is expected to rise as investment in environmental management increases and more municipal wastewater is treated to even higher standards [2]. The corresponding improvement in the environmental impact of water resources is likely to be countered by a marked increase in sludge volumes produced. In terms of high production volumes, both current and forecasted, the convenient management of sludges produced at sewage plants is a fundamental requirement.

While there are several ways of disposing of sewage sludge, considered use of this waste material

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can turn it into a resource. Much research has focussed on the use of sludge as an organic fertiliser in agricultural applications [3], which ideally could be a very attractive option. However, there are some important limitations, which are mainly related to aspects such as sludge quality, appropriate soil availability and difficulties encountered in its management and monitoring. Although other alternatives for this residue exist, a large proportion of the sludge produced is not valorised but is rejected together with other residues in waste tips. The necessities of investigating possible innovative routes are obvious for sewage sludge valorisation. Of these, those presented in this paper aim to study the potential application of activated carbons made from sewage sludge in aqueous stream purification.

Almost any carbonaceous material can be used as a precursor to activated carbons [4]. In practice, inexpensive materials are preferred, considering that the final product properties will differ, depending not only on the raw material used but also on the activating agent used and the conditions of the activation process. Taking into account factors such as the presence of volatile components and the fact that sewage sludge is carbonaceous in nature, this material may be considered as potentially suitable for the production of activated carbon if it is pyrolysed under controlled conditions and/or with some chemical treatment. Recently, several investigations have shown the feasibility of this conversion [5–10].

As activated carbons are obtained from materials with a high carbon content, they display high adsorption capacity, which is determined by the porous structure of the carbon. Due to this high adsorption capacity, activated carbons are very useful in mixture separation and liquid purification [11]. Nevertheless, from a practical point of view, the high cost of activated carbon presents a major drawback to these applications, especially in the field of industrial effluent treatment where activated carbons may play a very useful role. Disposal of industrial wastewaters poses a major environmental problem because such effluents contain various contaminants that are usually difficult to remove due to them being resistant to conventional biological methods. Liquid-phase

adsorption has been shown to be a promising option for the removal of non-biodegradable organic pollutants from aqueous streams, activated carbons being the most common adsorbent for this process due to their effectiveness and versatility [7].

The use of sewage sludge to remove contaminants present in wastewater would offer both a management option for sewage sludge and also provide residue valorisation as a low-cost precursor for activated carbon production. As the costs incurred by a sewage plant in the treatment of sludges represent an important percentage of total costs [12], the use of these sludges in the treatment of waters entering the plant itself would reduce costs.

When characterising an active carbon, although the most standardised procedure is determination of the N_2 -BET value [13], characterisation must be carried out depending on its planned utilisation [14]. In order to characterise the adsorption power of activated carbons, their adsorption capacity for different adsorbates has to be considered bearing in mind that depending on their origin and treatment history, they may behave differently.

In this research work, in order to study adsorbent behaviour in the liquid-phase, batch adsorption tests were undertaken; commercial dyes and phenol were the chosen adsorbates. Dyeing industry effluents constitute one of the most problematic wastewaters to be treated not only in terms of their toxic content but also for colour, which, because visible to human eye, is the first contaminant to be seen. In contrast, phenol has been extensively used in adsorbent characterisation studies, since it provides information on the feasibility of using adsorbents for the treatment of wastewaters [4]. Aqueous solutions containing commercial dyes and phenol were magnetically agitated with the prepared adsorbents, so the affinity of the different compounds for the adsorbents could be determined. All adsorption tests were undertaken in two subsequent stages, namely kinetic experiments were carried out first to obtain adsorption isotherms for each of the adsorbates and then, binary mixtures of adsorbates were agitated together with the sewage sludge based activated carbons. The adsorptive capacity achieved

for a certain compound is usually modified by the presence of other adsorbates; preferential adsorption is then visible.

Mass transfer has to be considered when considering the removal of organic pollutants from aqueous solution. Diffusion of the adsorbate is not as fast as for gases and so the adsorbent particle size may influence adsorbate mass transfer [14]. Adsorbents with a small particle size are preferably used for adsorption from solution phase because they present a large surface area and a small diffusion distance. However, considerable effort may be required to achieve small particle sizes. Adsorption tests have were carried out using particles of activated carbon at varying diameter to determine the effect of particle size on adsorption.

2. Material and methods

2.1. Preparation of the adsorbents

The sludges used in this study came from an urban plant in which biological wastewater treatment by activated sludge is carried out. Sewage sludge collected both from the primary decanting step and the aerobic biological stage was later submitted to anaerobic stabilisation at this plant.

Adsorbent materials from sewage sludge were produced by chemical activation by H₂SO₄ impregnation followed by pyrolysis. The parent sludges were initially oven dried at 105 °C to constant mass and the dried sludges were then ground to approximately 1 mm in diameter particles. At this stage, chemical activation was undertaken by impregnating the sludges with H₂SO₄ in a 1:1 by mass proportion. Sludge was kept in contact with the acid over 48 h in a continuously mixed reactor. The ensuing activated sludges were then pyrolysed under inert nitrogen, with a heating rate of 40 °C min⁻¹ up to 625 °C with a dwell time of 30 min at this temperature. After pyrolysis, the particles were washed with dilute HCl (10% by mass) to remove remaining activating agent. Finally, after oven drying at 80 °C, the resultant materials were ground and sieved to obtain particles with a diameter between 0.12 and 0.5 mm. These adsorbent particles were submitted to further grinding to secure a fraction of diameter < 0.12 mm. The final adsorbent materials have been referred to as ASS (activated sewage sludge) and the particle size has been labelled g2 (0.12 < diameter < 0.5 mm) and g1 (diameter < 0.12 mm). To study the influence of chemical activation on active carbon production from sewage sludge, samples which had been submitted only to the pyrolysis step were also used in batch adsorption tests, so that any increased adsorptive capacity could be associated to the activation process. These non-activated samples were designated by PSS (pyrolysed sewage sludges), their particle size being equal to the so-called g2 (0.12 mm < diameter < 0.5 mm).

Although the effect of activation and consequent porosity development upon the adsorption capacity of the materials was later determined using liquid adsorption tests, a textural characterisation of the adsorbents prepared from urban sewage sludges was first carried out. Gases adsorption measurements are frequently used for the surface area determination and the pores size distribution [13]. The relationship, at a constant temperature, between the quantity of gas adsorbed and the gas equilibrium pressure constitutes the adsorption equilibrium. The adsorption isotherms of CO_2 at 273 K and of N_2 at 77 K are normally used for materials characterisation. For this research work, these adsorption isotherms were obtained by means of a Gemini 2375 porosimeter in the case of CO₂ and in an ASAP 2010 apparatus for the N₂, both instruments from Micromeritics. With regard to the N₂ adsorption, the method of Brunauer-Emmet-Teller (BET) based on nitrogen adsorption is the standard procedure most commonly used for the determination of the surface area [15]. Activated sludges gave off BET $(N_2, 77 \text{ K})$ values about 390 m² g⁻¹ and the value of C, which reflects the energy of the interaction adsorbent-adsorbate, was higher than 100, which indicates that the surface area calculus have a theoretic consistency. The BET (N₂, 77 K) value obtained was of the same order as those previously presented by other authors, such as the 309 m² g⁻¹ obtained by Lu [8], upon ZnCl₂-activation of sludge or the 261 m²g⁻¹ obtained by Martin et al. [8], upon activation with H_2SO_4 . For the non-activated but pyrolysed sludges, BET $(N_2,$ 77 K) values measured were around 80 m² g⁻¹ (C > 100), which reflects the positive influence of activation on porosity development.

2.2. Single adsorption tests

Crystal violet and indigo carmine were the two dyes used in the present research work. Crystal violet has been previously used in adsorption tests [7] and is a toxic pigment used as a fungicide and also in the Microbiology field. Indigo carmine is used as a colouring additive in the pharmaceutical and food industries and also in medicine. Phenol has also been employed in this study, since, together with its by-products, it is a very important

organic pollutant that is common in industrial wastewaters [16]; in addition, phenolic compounds have a similar structure to some insecticides and herbicides which are not biodegradable. These three adsorbates are difficult to remove from wastewater and are quite resistant to conventional biological treatments. The respective structures of these compounds appear in Fig. 1, their properties being listed in Table 1. Water solutions of these compounds were prepared taking into account the purity of each product, all of them having being got from Merck.

Adsorption tests under magnetic stirring were conducted in two steps; firstly a kinetic study was undertaken to determine equilibrium times and

Indigo carmine
$$\begin{array}{c} C_{rystal} \\ C_{1_0}H_8N_2Na_2O_8S_2 \\ \hline \\ O \\ \\ O \\ \hline \\ O \\ \\ O$$

Fig. 1. Phenol (P), crystal violet (CV) and indigo carmine (IC) molecular structures.

Table 1 Properties of the compounds employed for the adsorption tests

Adsorbate	Molecular formula	Molar mass (g mol ⁻¹)	Purity (%)	Water solubility (g l ⁻¹)	λ _{max} (nm)
Crystal violet	C ₂₅ H ₃ ClN ₃	407.99	90	10 (25 °C)	586
Indigo carmine	$C_{16}H_8N_2Na_2O_8S_2$	466.36	80	82 (20 °C)	609
Phenol	C_6H_6O	94.11	99.5	16 (25 °C)	270

results were then used to define further tests to be conducted in order to build the adsorption isotherms.

Kinetic tests were undertaking in discontinuous and the adsorbent was magnetically stirred in 100 ml of a solution in a series of 250 ml Erlenmeyer flasks closed to avoid evaporation. The initial concentration of the corresponding adsorbate was 100 mg l⁻¹, the adsorbent/adsorbate solution ratios being kept at 5 g l⁻¹. Residual adsorbate concentration was monitored by periodically removing the Erlenmeyer flasks at increasing time intervals ranging from 15 min to 14 h. The residual concentration of each adsorbent was determined using a Beckman UV/vis spectrophotometer (Model DU620) and in a silica cuvette. Prior to the concentration analysis, calibration curves were established for each compound at the wavelength at which each of them showed a maximum of light absorbance when solved in water, these wavelengths appear in Table 1. The corresponding adsorption kinetics curves were obtained and the equilibrium time was were graphically determined from these curves as the time needed to reach a 99% of the maximum adsorption level in each

Adsorption isotherms (25 ± 2 °C) were obtained by magnetically stirring the adsorbent in solutions of varying adsorbate concentration and for a period of time equal to the respective equilibrium times. The range of the initial adsorbate concentrations in solution was $100-1000 \text{ mg l}^{-1}$, residual concentrations being determined as described above.

2.3. Mixed adsorption tests

For testing the preferential adsorption by the adsorbents produced from sewage sludge mixed adsorption tests were carried out. The aim was to study the competition between the adsorbates when using binary mixtures (in 1:1 initial adsorbate proportion) as starting solutions.

Adsorption isotherms (25 ± 2 °C) were obtained by magnetically stirring the adsorbent in solutions varying concentration. This concentration was in the range 100-1000 mg 1^{-1} for each of the adsorbates in the indigo carmine-phenol binary mixture

and in the range 100–3000 mg l⁻¹ for indigo carmine–crystal violet and crystal violet–phenol, as it was observed that the presence of crystal violet in the mixture increased the adsorptive capacity. Each mixed solution was stirred during a period of time long enough to reaching the adsorption equilibrium for both the adsorbates present in the mixture. The residual concentrations in the mixed adsorption tests were spectrometrically determined as described above. Nevertheless for each compound another calibration at the corresponding wavelength was to be done so to weigh up the light absorbance of the other adsorbate present in the mixture at that wavelength.

3. Results and discussion

3.1. Single adsorption tests

Kinetic tests were undertaken to determine the stirring time needed for each of the samples to reach an equilibrium point with regard to the amount of each compound adsorbed. The kinetic curves corresponding to each of the compounds adsorbed by each of the adsorbent samples are shown in Fig. 2. From these curves the equilibrium times were determined and, as can be seen in Table 2, although the equilibrium times (t_{eq}) corresponding to the smallest particle size (g1) are slightly shorter, no remarkable differences were found between the two particle size fractions of the same sample when this had been chemically activated. Equilibrium times were dependent on the adsorbate to be retained, so it has been observed that phenol adsorption occurs more slowly than indigo and specially crystal violet adsorption. Samples only pyrolysed needed longer periods of stirring before equilibrium except for phenol, which total uptake was so small that the adsorbent got saturated quite promptly.

As can be seen in Fig. 2, when using the sludge based prepared adsorbents in batch tests, the concentration in the solution of each of the compounds considered decreased continuously along time until an equilibrium point was reached, characteristic both of each sample and each adsorbate. After reaching the equilibrium point, a

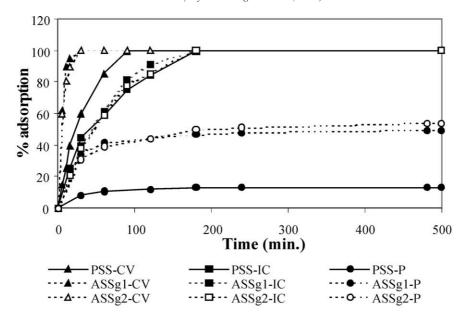


Fig. 2. Kinetic curves for the adsorption of phenol (P), crystal violet (CV) and indigo carmine (IC) adsorption by sewage sludge based activated carbons, namely ASS-g1 (particle diameter < 0.12 mm), ASS-g2 (0.12 < particle diameter < 0.5 mm) and PSS-g2 (0.12 < particle diameter < 0.5 mm).

prolonged contact time under stirring did not result in further adsorption. It has been seen that the particle size in the range of 0.12–1.5 mm may affect on the adsorption process kinetics [5], small particle sizes favouring the transferring of adsorbate inside the particle pores towards their inner surfaces and further surface diffusion into more internal pores. Nevertheless, in the present study the two different adsorbate particle sizes used must be small enough so not to affect the adsorption process to a high extent.

The sludge-derived adsorbents have exhibited a higher adsorption capacity for crystal violet than

Table 2 Time needed, in seconds, for reaching the equilibrium ($t_{\rm eq}$) by the ASS and PSS samples when considering each of the adsorbates uptake along time during the adsorption tests

Adsorbent	Particle size	Crystal violet $t_{\text{eq min}}$	Indigo carmine $t_{\rm eq\ min}$	Phenol t _{eq min}
ASS	g1 g2	20 25	165 175	260 300
PSS	g2	90	180	120

for indigo carmine or phenol. For the adsorbates studied no adsorptive capacity difference can be related to the adsorbent particle size as it can be seen by comparing Fig. 3 to Fig. 4. Being the two adsorbent particle sizes used below 0.5 mm, neither total adsorbate uptake neither equilibrium have shown a marked dependence on this fact. Nevertheless, we could assume that particle size affects less on the adsorption level than on the process kinetics.

Residual adsorbate concentration was measured when starting from solution with different concentrations and after adsorbent/adsorbate contacting periods equal to the equilibrium times previously determined. Figs. 3 and 4 illustrate the adsorption levels reached upon adsorption from solution by representing each adsorbate uptake (q_e) by each sample of activated carbon (ASS) against adsorbate initial concentration (C_i) in solution.

The adsorption data would correspond to isotherms of type I [15], i.e. convex upward curves, considered as corresponding to strong adsorption. Results obtained for each adsorbate adsorption $(q_e \text{ in mg of adsorbate/g of adsorbent})$ starting at

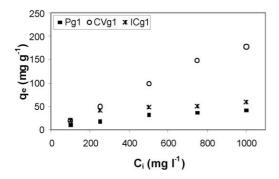


Fig. 3. Phenol (P), crystal violet (CV) and indigo carmine (IC) adsorption by sewage sludge based activated carbons when using ASS-gl particles with a diameter <0.12 mm.

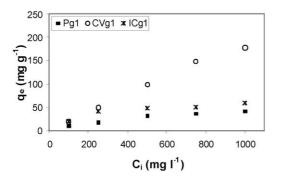


Fig. 4. Phenol (P), crystal violet (CV) and indigo carmine (IC) adsorption by sewage sludge based activated carbons when using ASS-g2 particles with a diameter between 0.12 and 0.5 mm.

different initial concentrations against residual adsorbate concentration in the equilibrium (C_e in mg of adsorbate/l of solution) were fit to two adsorption isotherms models, those of Langmuir and Freundlich.

The Langmuir Eq. (1) is based on a theoretical model and assumes that the maximum adsorption corresponds to a monolayer saturated with adsorbate molecules on the adsorbent surface, which is energetically homogeneous from the adsorptive point of view. On the contrary, the Freundlich proposal (2) is an empirical model that considers heterogeneous adsorptive energies on the adsorbent surface.

$$q_{\rm e} = \frac{Q \cdot K_L \cdot C_{\rm e}}{1 + K_L \cdot C_{\rm e}} \tag{1}$$

where Q is a constant relative to the adsorptive capacity and K_L a parameter which makes reference to the adsorption energy.

$$q_e = K_F \cdot C_e^{1/n} \tag{2}$$

where the K_F parameter is relative to the adsorption capacity and n makes reference to the process intensity.

Fittings obtained for both models are shown in Table 3, reflecting the corresponding coefficients of determination together with the values of the characteristic parameters for both models studied.

Table 3
Results from fittings of the isotherms of adsorption of crystal violet (CV), indigo carmine (IC) and phenol (P) by the ASS and PSS to Langmuir and Freundlich models

Adsorbent	Particle size	Adsorbate	Fitting to the Langmuir model		Fitting to the Freundlich model			
			C.D.	K_L (l mg ⁻¹)	Q_{max} (mg g ⁻¹⁾	C.D.	$K_F (\text{mg g}^{-1} \text{mg}^{-1/n})$	n
ASS	g1	CV	0.9594	0.63	263.22	0.9815	101.25	8.34
		IC	0.9529	0.04	60.04	0.9597	25.37	8.20
		P	0.9698	0.02	42.04	0.9748	6.33	3.51
ASS	g2	CV	0.9543	0.56	270.88	0.9807	99.69	8.06
		IC	0.9541	0.06	54.38	0.9570	29.04	11.28
		P	0.9477	0.04	29.46	0.9571	13.91	9.87
PSS	g2	CV	0.9752	0.01	184.68	0.9900	15.63	3.31
	-	IC	0.8903	0.03	30.82	0.8906	14.16	8.59
		P	0.9245	0.06	5.56	0.9253	4.25	29.60

C.D. = coefficient of determination of the fitting. K_L and Q_{max} = characteristic parameters of the Langmuir model. K_F and n = characteristic parameters of the Freundlich model.

It has to be noted that Freundlich parameters are only descriptive whereas Langmuir parameters intend to have a real physical meaning.

As previously seen in different experiments and also with different adsorbates [17] adsorptive capacities obtained by the pyrolysed sludges (PSS) were poorer than for those chemically activated, this showing the effectiveness of the activation. Crystal violet uptake by pyrolysed sludge (180 mg g⁻¹) was about a 65% of the obtained by the activated samples (ASS), indigo carmine (30 mg g⁻¹) around the 50% and phenol (5 mg g⁻¹) approximately the 15% of the ASS adsorptive capacity.

About adsorption isotherms for data corresponding to the three samples considered, Freundlich model appears to provide slightly more reasonable fittings than the Langmuir one. The Langmuir equation has been found to give poor fits for adsorption tests using sewage sludge activated carbons [5,6], which could be related to these materials not following the assumption of surface energetic homogeneity by this model, an assumption not accepted in the frame of the Freundlich model.

3.2. Mixed adsorption tests

Binary solutions in which adsorbate proportion was 1:1 were submitted to stirring together with the chemically activated sewage sludges. Figs. 5–10 show each of the two adsorbates uptake by the adsorbent (q_e) against its individual initial concentration (C_i) . Total adsorption by the adsorbent samples from each of the binary solutions is also represented in these figures to make it possible to compare total uptake depending on the solutes present in the binary.

Figs. 5 and 6 show indigo carmine and phenol competitive adsorption. Although these adsorbates uptake have been quite poor, indigo carmine seems to be preferred to phenol by the produced adsorbents. Both Indigo carmine and phenol adsorption when they are together in solution have been lower than their adsorption from pure solution. The adsorption of each of them from their mixed solution is around half their respective adsorptions by separate. Total adsorption is

nearly the same order to each individual one, as can be seen Figs. 3 and 4.

Crystal violet and phenol adsorption results from binary solution are shown in Figs. 7 and 8. As it could be expected from pure experiments,

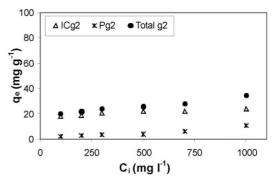


Fig. 5. Indigo carmine (IC) and phenol (P) adsorption from binary solution by sewage sludge based activated carbons when using ASS-g1 particles with a diameter <0.12 mm.

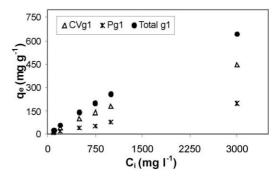


Fig. 6. Indigo carmine (IC) and phenol (P) adsorption from binary solution by sewage sludge based activated carbons when using ASS-g2 particles with a diameter between 0.12 and 0.5 mm.

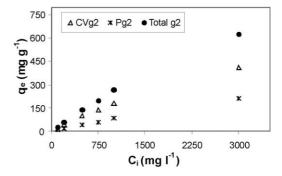


Fig. 7. Crystal violet (CV) and phenol (P) adsorption from binary solution by sewage sludge based activated carbons when using ASS-gl particles with a diameter <0.12 mm.

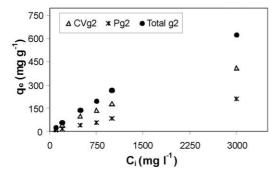


Fig. 8. Crystal violet (CV) and phenol (P) adsorption from binary solution by sewage sludge based activated carbons when using ASS-g2 particles with a diameter between 0.12 and 0.5 mm.

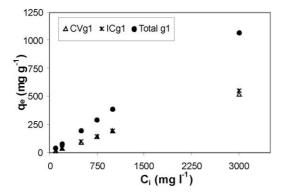


Fig. 9. Crystal violet (CV) and indigo carmine (IC) adsorption from binary solution by sewage sludge based activated carbons when using ASS-g1 particles with a diameter <0.12 mm.

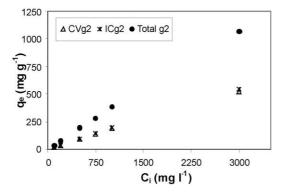


Fig. 10. Crystal violet (CV) and indigo carmine (IC) adsorption from binary solution by sewage sludge based activated carbons when using ASS-g2 particles with a diameter between 0.12 and 0.5 mm.

crystal violet uptake has been much higher than this corresponding to phenol. It deserves special attention that, considering their individual initial concentrations, both crystal violet and phenol adsorption has been higher than in the pure tests (Figs. 3 and 4). Crystal violet adsorption has been enhanced up to around two and a half times the adsorption in the pure tests. The adsorption of phenol is nearly five the adsorption got in the pure tests. Summing up these adsorbates retention, total removal by the sewage sludge based activated carbons is very high, reflecting a great adsorption capacity.

Results corresponding to the adsorption of crystal violet and indigo carmine from mixed solution are shown in Figs. 9 and 10. Each compound adsorption referred to its individual initial concentrations appears enhanced comparing to this adsorbates uptake corresponding to the pure tests. The adsorption of indigo carmine is about nine times higher in the binary than in the individual test while this of crystal violet arose to be nearly three times higher. Resulting total adsorption is even higher than that previously shown (Figs. 7 and 8) corresponding to the crystal violet and phenol solution.

Being the adsorbent affinity for crystal violet very high, both indigo carmine and phenol adsorption have increased when they are in solution with crystal violet. Nevertheless, indigo carmine and phenol together in solution has not favoured their respective adsorption by the activated carbons produced. It seems that the crystal violet presence in solution enhances anyway the trend to be adsorbed by the sewage sludge based activated carbons. The surface of activated carbons is believed to be negatively charged as a consequence of the presence of acidic functional groups [14] and this has also been found for sewage sludge derived activated carbons [7]. Therefore this enhanced adsorption may be related to the marked cationic properties of crystal violet, which are originated from positively charged atoms and so the surface of the adsorbent particles. On the other hand, apart from a possible multilayer adsorption favoured by crystal violet molecules, total initial concentration in solution must be taken into account with regard to the enhanced adsorption in binary experiments. It has been checked by increasing initial concentrations up to 4000 mg l⁻¹ in pure solutions that, specially for crystal violet and indigo carmine, adsorption reaches higher levels, equilibrium forces favouring this to occur. When adsorption is positive, a higher uptake corresponds to a higher amount of molecules to be adsorbed in solution, no matter their respective initial concentrations but total concentration. Anyway, competition between adsorbates is going to take place in binary tests so each adsorbate adsorption will depend on the adsorbent preference. Indigo carmine and phenol removal from solution were lower than this of crystal violet in pure adsorption tests, not increasing in binary tests since neither of them favour adsorption.

Finally, it has to be said that no significant differences related to the adsorbent particle size have been found in none of these mixed adsorption tests. Therefore it could be presumed that both particle sizes employed offer similar resistance to the adsorbate mass transfer.

4. Conclusions

Materials with adsorbent properties have been produced from sewage sludge, chemical activation being a key step of the process. Comparing the adsorptive capacities of the only pyrolysed sewage sludge and those that had been previously impregnated with sulphuric acid, it may be said that activation has achieved its objective of enhancing the creation of pores and its enlargement during the carbonisation.

The produced activated carbons were characterised by their surface area and porosity showing that these materials possessed a remarkable BET-N₂ surface area. On the other hand, these sewage sludge based activated carbons have been able to remove from solution organic compounds such as crystal violet, indigo carmine and phenol. Both the adsorption kinetic studies and the isotherm determination indicate that the adsorbents produced behave different depending on the compound to be removed from solution. All isotherm adsorption data were found better fitted by the

Freundlich model than the Langmuir equation, best fittings having been got for crystal violet adsorption. On the other hand, the sewage sludge based activated carbons seem to have a great affinity for crystal violet, its adsorption occurring faster an reaching higher levels than for indigo carmine or phenol.

Preferential adsorption under competition conditions has been studied by binary adsorption tests in which two of the above adsorbates in solution were stirred together with the activated carbon produced. Total adsorption carried out by the sewage sludge derived adsorbents has been considerable from those mixed solutions in which crystal violet was present, uptake being approximately 1000 mg g⁻¹ of adsorbent from these binary solutions. In these cases also individual adsorbate removal has been enhanced compared to its adsorption from previous pure experiments. Crystal violet presence and total increased concentration in solution may have favoured molecules adsorption on the adsorbent particles surface, this fact being interesting to be considered when thinking about a practical application.

Adsorption results have not been significantly modified by the adsorbent particle sizes used for the tests performed, both under 0.5 mm. It could be assumed therefore that problems related to mass transfer are similar when using these two particle sizes of the adsorbent produced for the removal of the adsorbates considered.

Further work should be carried out to characterise better the adsorptive behaviour of activated carbons, studying other pollutants adsorption from solution both separately and under competition and taking into account facts such as the adsorbates molecular size, charge and possible interactions to a surface level.

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