



Tartrazine modified activated carbon for the removal of Pb(II), Cd(II) and Cr(III)

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ABSTRACT

A two in one attempt for the removal of tartrazine and metal ions on activated carbon has been developed. The method was based on the modification of activated carbon with tartrazine then its application for the removal of Pb(II), Cd(II) and Cr(III) ions at different pH values. Tartrazine adsorption data were modelled using both Langmuir and Freundlich classical adsorption isotherms. The adsorption capacities q_m were 121.3, 67 and 56.7 mg g⁻¹ at initial pH values of 1.0, 6.0 and 10, respectively. The adsorption of tartrazine onto activated carbon followed second-order kinetic model. The equilibrium time was found to be 240 min at pH 1.0 and 120 min at pH 10 for 500 mg L⁻¹ tartrazine concentration. A maximum removal of 85% was obtained after 1 h of contact time. The presence of tartrazine as modifier enhances attractive electrostatic interactions between metal ions and carbon surface. The adsorption capacity for Pb(II), Cd(II) and Cr(III) ions has been improved with respect to non-modified carbon reaching a maximum of 140%. The adsorption capacity was found to be a pH dependent for both modified and non-modified carbon with a greater adsorption at higher pH values except for Cr(III). The enhancement percent of Pb(II), Cd(II) and Cr(III) at different pH values was varied from 28% to 140% with respect to non-modified carbon. The amount of metal ions adsorbed using static regime was 11–40% higher than that with dynamic mode. The difference between adsorption capacities could be attributed to the applied flow rate.

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1. Introduction

Activated carbon has been widely used in the environmental pollution control, as an adsorbent for the removal of organic compounds and heavy metal ions from industrial effluents. When used, without any surface treatment, activated carbon present an adsorption capacity for metal ions from fair to as low to none, due to the fact that metal ions often exist in solution either as ions or as hydrous ionic complex [1,2]. This observation has led many investigators to develop different kinds of surface treatments such as oxidative and non-oxidative methods in an attempt to modify the interfacial region by increasing surface functional groups and hence, improving its potentially low adsorption capacity [3–8]. Being mechanically robust, highly hydrophobic and having exceptionally high surface area, molecules with large hydrophobic groups can be strongly adsorbed onto its surface and alter its characteristics. Several research groups [9–16] have studied the non-oxidative surface modification, including immobilisation, anchoring and grafting of organic molecules, which has gained a considerable attention in recent years. Among these, Ucer et al.

[11,12] have investigated the immobilisation of tannic acid onto activated carbon and the evaluation of its capacity for the removal of metal ions. Their result indicated that modification with tannic acid has improved metal ions uptake. Previously [17–19], we have investigated the elimination of heavy metals and phthalate from industrial phosphoric acid and wastewater on sodium diethyldithiocarbamate (SDDC) and sodium dodecylsulfonate (SDS) and metal ion-modified activated carbon, and found a higher elimination capacity for the modified carbon than the plain one. Other methods to introduce suitable functional groups in tentative of enhancing the adsorption capacity of activated carbon have been thoroughly investigated and discussed in a recent published review [20].

The colour additives tartrazine was selected as a model for this study because in addition to its widespread use in food products, drugs, cosmetics, pharmaceuticals and for dyeing of some textile fibres, its chemical structure contains sulfonate groups that could enhance attractive electrostatic interactions with metal ions. Food, dyeing, pharmaceutical, electroplating and other industries could benefit from this technique, as it has two advantages in one application. The first advantage could be applied for the removal of sulfonate dyes from dyeing process wastewater and the second will be applied to the removal of metal ions from electroplating wastewater. Further advantage of fixed-bed modified columns are,

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reducing chemical consumption; eliminating sludge disposal and recycling the 'cleaned' wastewater back to the production area.

Therefore, this work will have two in one objectives; the first will be conducted on the immobilisation of tartrazine, so its elimination and the second, will be used to eliminate positively charged species such as lead, cadmium and chromium by binding to the coupling agent. According to our knowledge no work has been done for the removal of metal ions on tartrazine-modified carbon, however, much work has been carried out on the removal of tartrazine using different adsorbents such as: bottom ash, de-oiled Soya [21], hen feathers [22] and chitin products [23].

To evaluate the efficacy of activated carbon on the adsorption of tartrazine and hence the removal of metal ions, different experimental parameters such as pH and concentrations were investigated using static and dynamic regimes. The study was completed by evaluating the performance of tartrazine-modified carbon for the removal of Cd, Pb and Cr(III) from synthetic wastewater.

2. Experimental

2.1. Reagents

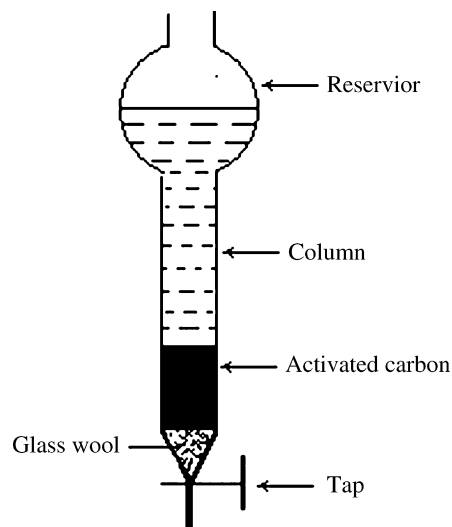
The activated carbon used in this study was obtained from Fluka (Flucka, France) with a particle size of 100–150 μm and a specific surface area of 1100 m^2g^{-1} . Analytical grade tartrazine, trisodium-5-hydroxy-1-(4-sulfonatophenyl)-4-(4-sulfonatophenylazo)-H-pyrazole-3-carboxylate ($\text{C}_{16}\text{H}_9\text{N}_4\text{Na}_3\text{O}_9\text{S}_2$, molecular weight 534.4) was obtained from Merck. All other chemicals used were of AR grade. Throughout the studies all the solutions including tartrazine, Cd, Pb and Cr(III) stock solutions (500 mgL^{-1}) were prepared in distilled water. Experimental solutions at the desired concentration were then obtained by successive dilutions. The initial pH was adjusted with solutions of NaOH or HNO_3 .

2.2. Adsorption of tartrazine onto activated carbon

The adsorption experiments were carried out in batch mode by adding 1.0 g of activated carbon to 100 mL of a tartrazine solution at known concentration (20–500 mgL^{-1}) and pH (1–12) in a 250 mL Erlenmeyer flask. These samples were agitated for 24 h at 25 °C. After equilibrium was attained, all samples were filtered and the residual concentration of tartrazine was measured by UV-vis spectrophotometry (Beckman, DU 640B) at 430 nm. The calibration curve was linear in the range of 10–100 mgL^{-1} . The amount of tartrazine was determined from the difference in concentrations at the beginning and end of each batch test.

2.3. Procedure of column packing

For the column operations (Scheme 1), a slurry of plain activated carbon (0.5 g) and tartrazine-modified carbon (0.5 g) was packed in glass columns (200 mm long \times 10 mm i.d.). To avoid air entrapment, the column was first filled with water then the slurry of each adsorbent was introduced carefully in each column, which slowly settles down by displacing the heel of water. Metal ion solutions of particular concentrations were then allowed to percolate through each column at a flow rate of 0.5 mLmin^{-1} . Samples were collected at the outlet of the column until the column reached saturation and then they were analysed by atomic absorption spectrophotometer (PerkinElmer, Analyst 300) and polarographic techniques (MDE 150, Radiometer, France). The breakthrough curves were determined from these experiments.



Scheme 1. Schematic diagram of the purification column.

3. Results and discussion

3.1. Equilibrium kinetics

3.1.1. Effect of contact time

The initial concentrations of tartrazine and the amount of activated carbon used were kept constant for kinetic studies of the adsorption process at different pH in order to make a comparative study. As shown in Fig. 1 the rate of removal of tartrazine was rapid initially and then slowed down gradually until it attained an equilibrium beyond which there was no significant increase in the rate of removal. The initial rapid adsorption was perhaps due to participation of specific functional groups, macro- and micropores and active surface sites in the adsorptive removal of the tartrazine molecules. A large fraction of the tartrazine was removed within a few minutes (20 min). Tartrazine removal increased gradually to reach approximately 102 mg g^{-1} (85%) at the end of 1 h contact time and remained more or less constant at around 121 mg g^{-1} even after a contact time of 24 h. It could be concluded that the ongoing adsorption is sufficiently rapid to recommend their use in the treatment of wastewater polluted by tartrazine.

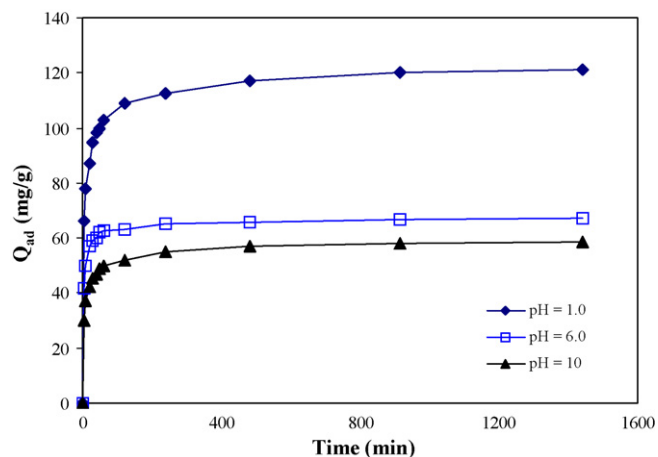


Fig. 1. Equilibrium time of tartrazine adsorption onto activated carbon at different pH. Adsorption experiments were carried out in batch mode using 1.0 g of activated carbon and 100 mL of tartrazine (200 mgL^{-1}).

Table 1
Kinetic parameters of tartrazine adsorption

pH	$q_m(\text{exp})$ (mg g ⁻¹)	Second order		
		k_2 ($\times 10^{-3}$ g mg ⁻¹ min ⁻¹)	$q_m(\text{cal})$ (mg g ⁻¹)	r^2
1	121.3	76.236	121.9	0.999
6	67	6.627	67.1	1.000
10	56.7	1.906	57.8	0.999

3.1.2. Kinetic of tartrazine adsorption

In order to predict the adsorption data of tartrazine as function of time, two kinetic models were tested: a pseudo-first-order and a pseudo-second-order. According to Namasivayam and Kadirvelu [24] and Gupta et al. [25] the first-order model can be expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

where q_e and q_t (both in mg g⁻¹) are the solute amounts adsorbed per unit mass of adsorbent at equilibrium and at time t (min), respectively, k_1 (min⁻¹) is the adsorption rate constant. The values of k_1 and q_e are determined from the slope and the intercept of the plots of $\ln(q_e - q_t)$ versus t , respectively. According to Ho et al. [26] the kinetics of adsorption can be represented by a pseudo-second-order model:

$$\frac{dq_t}{dt} = k_2(q_e - q_t) \quad (2)$$

where k_2 is the pseudo-second-order rate constant (g mg⁻¹ min⁻¹). For the boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$, the integrated form of Eq. (2) becomes

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (3)$$

Eq. (3) can be rearranged to obtain Eq. (4), which has a linear form

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

An adequate pseudo-second-order kinetics model should show a linear plot of t/q_t versus t . The value of q_e is easily deduced from the slope of the plot of t/q_t versus t . Once q_e was identified, the value of k_2 can be obtained either from the intercept of the plot or from $t_{1/2}$ (half-adsorption time). The latter method based on the half-adsorption time proved to be more reliable and accurate. The half-adsorption time is the time required to uptake half of the maximal amount of tartrazine adsorbed at equilibrium.

The evolution of the adsorption data of tartrazine at different pH and as a function of time are illustrated in Fig. 1. It appears from Fig. 1 that for all the experiments a rapid initial rise of the adsorption capacities q_t and the equilibrium is almost reached within 240 min. The validity of the kinetic models is tested by the magnitude of the regression coefficient r^2 , given in Table 1. It is important to note that for a pseudo-first-order model, the correlation coefficient is always less than 0.90, which is indicative of a bad correlation. Therefore, the pseudo-first-order model is not suitable for modelling the adsorption of tartrazine onto activated carbon. In contrast, the application of a pseudo-second-order model leads to much better regression coefficients, all greater than 0.99. Furthermore, the experimental and calculated values of q_e are very close, as indicated in Table 1, thus, the pseudo-second-order kinetic model is well suitable to model the adsorption curves of tartrazine onto activated carbon.

3.1.3. Intraparticle diffusion studies

The adsorption kinetic data of tartrazine was further processed to identify the step that governs the overall removal rate in the

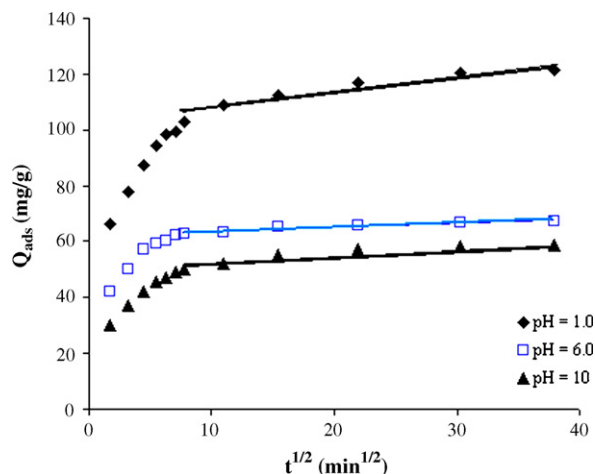


Fig. 2. Plots of fractions of tartrazine uptake against square root of contact time ($t^{0.5}$).

adsorption process. In general, adsorption may be described as a series of steps:

- transport of the tartrazine from the fluid to the external surface of the adsorbent across;
- the boundary layer (film diffusion);
- diffusion of tartrazine within the pores of the adsorbent (particle diffusion);
- adsorption itself onto the surface.

To determine whether particle diffusion is the rate-limiting step for tartrazine adsorption onto activated carbon, a plot of fraction of tartrazine uptake against square root of contact time ($t^{0.5}$) should be investigated. Some investigators [27,28] reported that if particle diffusion is involved in the adsorption process then a plot of tartrazine uptake versus the square root of time would result in a linear relationship. Moreover, the particle diffusion would be the rate-controlling step if this line passes through the origin.

The plots (Fig. 2) have the same general features, i.e. initial curved portion followed by final linear portion. The initial curved portions may be attributed to the boundary layer diffusion effect (liquid-film mass transfer), while the final linear portions may be attributed to intraparticle diffusion effects. From the figure, it may be observed that the straight line did not pass through the origin. This indicates that intraparticle diffusion is involved in the adsorption process but it is not the only rate-limiting mechanism and that some other mechanisms are involved. Such a deviation of the straight line from the origin may be due to the difference in the rate of mass transfer in the initial stage of adsorption [29,30]. The adsorption data indicate that the removal of the tartrazine from aqueous solution is rather complex process, involving both boundary layer diffusion and intraparticle diffusion; however, intraparticle diffusion appears to be the rate-limiting step in direct tartrazine uptake.

3.2. Adsorption isotherm

Adsorption isotherms are useful in understanding the adsorption interaction. The obtained equilibrium isotherm adsorption data was analysed using the Langmuir and Freundlich isotherm models. The experimental data for various studied pH were fitted better with the rearranged Langmuir isotherm model:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K} \quad (5)$$

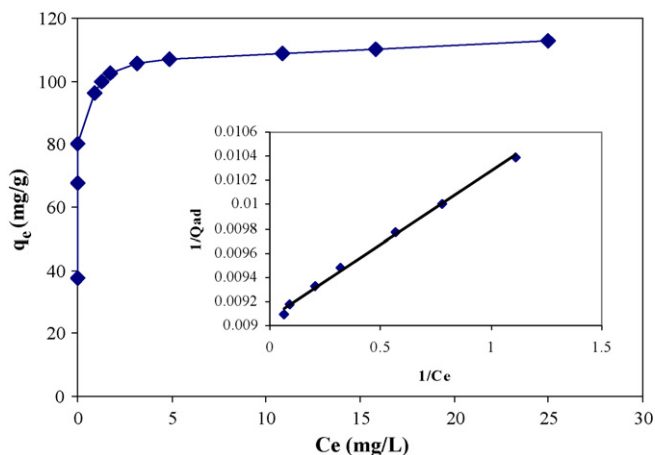


Fig. 3. Langmuir isotherm of tartrazine adsorption on activated carbon at pH 2.0. Adsorption experiments were carried out in batch mode using 1.0 g of activated carbon and 100 mL of tartrazine (20–500 mg L⁻¹). Samples were agitated for 24 h at 25 °C.

where q_m is the amount of solute adsorbed per unit mass of carbon corresponding to complete monolayer coverage and K is the Langmuir constant which is related to the affinity of the binding sites. A linear plot of (C_e/q_e) against C_e was employed to give the values of q_m and K from the slope and the intercept of the plot. The Langmuir adsorption isotherm of tartrazine on activated carbon at pH 2.0 (Fig. 3) gave a correlation coefficient higher than 0.99 with an equation of

$$\frac{C_e}{q_e} = 0.0012C_e + 0.0091 \quad (6)$$

The near unity regression coefficient value related to the Langmuir model indicates its good fit to tartrazine adsorption equilibrium data regardless of pH value and the formation of a monolayer over a homogeneous adsorbent surface.

3.2.1. Effect of pH on adsorption process

The effect of pH on the removal of tartrazine was investigated in the pH range from 1.0 to 12 at a temperature of 25 °C. The contact time has been fixed to 24 h for all the experiments. The experimental results are presented in Fig. 4. The adsorption was notably higher in the acidic medium than that of counterpart. This is caused by a high degree of surface protonation giving the anionic sulfonate groups a more favourable electrostatic force of attrac-

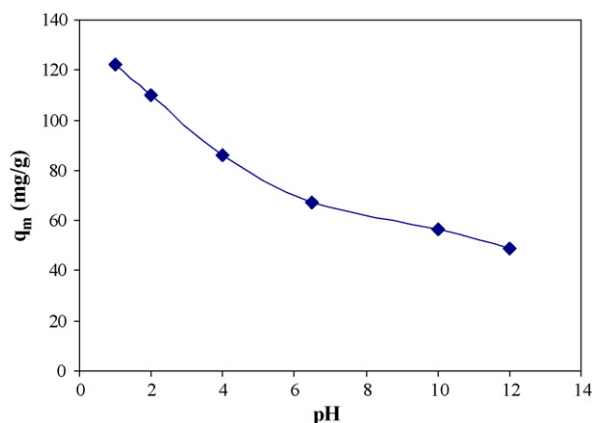


Fig. 4. Effect of the initial pH on the adsorption of tartrazine onto activated carbon. Experiments were carried out in batch mode using 1.0 g of activated carbon and 100 mL of tartrazine (200 mg L⁻¹). Samples were agitated for 24 h at 25 °C.

tion for the active surface. It is known that at pH values lower than pH_{pzc} , ($pH_{pzc} \sim 4.3$) the surface of activated carbon is positively charged. As the pH of the system increases, the number of positively charged sites decreases and the number of negatively charged sites increases, leading to a repulsion between anionic tartrazine and anionic surface. The electrostatic repulsion of the system has lowered the removal capacity from 121.3 mg g⁻¹ at pH 1.0 to 56.7 mg g⁻¹ at pH 10, with a loss of approximately 53% of its capacity in alkaline medium. Mittal et al. [21] studied the adsorption of tartrazine at different pH values on bottom ash and de-oiled Soya, they found a decline in percentage removal of dye at higher pH values. They explain this behaviour by the fact that an increase of protonation due to neutralization of negative charge at the surface of the adsorbents, which facilitates diffusion and provides more active surface of the adsorbents, resulting thereby greater adsorption at their surfaces. A decrease in the percentage removal with increase in pH may be due to deprotonation, which retards the diffusion.

However, the processes of tartrazine adsorption on activated carbon is not only determined by electrostatic interactions between sulfonate anions and the surface charge, but also by π - π dispersion interactions between the electrons of the activated carbon surface and the aromatic rings of tartrazine.

3.3. Removal of metal ions

The removal of metal ions by plain (NMC) and modified activated carbon (MC) have been investigated in a static and dynamic regimes. In both regimes, a single metal ion solutions with initial pH values of 2.0, 5.5 and 8.0 were tested. In an attempt to reach equilibrium in the dynamic regime, sufficient contact time between the mobile solution and the stationary carbon phase was recommended. Therefore, a column flow rate of 0.5 mL min⁻¹ was selected as a compromise between sampling cadence and equilibrium.

Metal ions removal capacity in dynamic regime was evaluated using the breakthrough curves. Results obtained (Figs. 5–7) show that these columns were effective in removing Pb(II), Cd(II) and Cr(III) ions from aqueous solutions. Removal capacities were higher with tartrazine modified activated carbon than plain once for all the studied metal ions. As known that pH is an important parameter in the adsorption process, therefore, the efficacy of these columns was tested at different solution pH. Figs. 5–7 show the influence of the solution initial pH on the removal of Pb(II), Cd(II) and Cr(III) ions on plain and tartrazine-modified carbon. It can be observed that the presence of tartrazine on the surface of activated carbon as modifier increased metal ions adsorption, regardless the pH considered. The adsorption capacity for Pb(II) has been increased with percentages that varied between 60% and 140% with respect to non-modified carbon. However, the adsorption percent of Cd(II) was varied from 36% to 140% and for Cr(III) from 28% to 56.6%. Further removal capacity enhancement was achieved at higher pH values for modified and non-modified carbon except for Cr(III) where a decrease in the removal capacity was observed (from 16.9 mg g⁻¹ at pH 5 to 13.3 mg g⁻¹ at pH 8). This behaviour can be explained by the charge of the metal species present and by the surface charge density at each pH value. The majority of the species studied presented a positive charge across the pH range studied. Therefore, the increased metal ions adsorption is due to the progressive ionisation of the surface functional groups. This implies an increase in the density of the surface negative charge due to the ionisation of plain carbon ($pH > pH_{pzc}$) in addition to the ionisation of tartrazine sulfonate groups, producing greater adsorption for Pb, Cd and Cr(III). However, the reduction in the adsorption of Cr(III) at pH values above 6, could be attributed to the repulsive electrostatic interac-

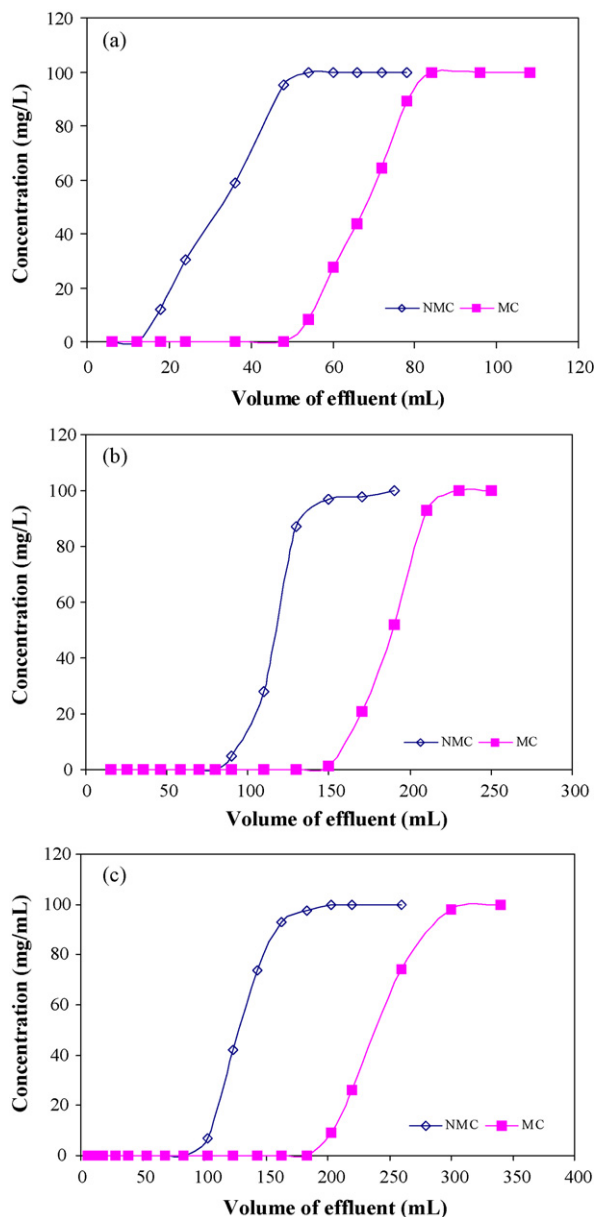


Fig. 5. Breakthrough curves of plain and tartrazine-modified carbon for Pb removal at different pH values. (a) pH 2; (b) pH 5; (c) pH 8. Columns (200 mm × 10 mm i.d.) were packed with 0.5 g modified and non-modified activated carbon. Samples (50 mg L⁻¹) were percolated with a flow rate of 0.5 mL min⁻¹.

tions established between surface charge and Cr species [Cr(OH)₄⁻] present at these pH values. Rivera-Utrilla et al. [16], have studied the effect of Cd(II), Cr(III) and Hg(II) on the adsorption of naphthalenetrisulfonic acid on activated carbon. They have found a greater adsorption when the charge signs of the metal species and sulfonate groups in the solution are opposite. In addition, they have observed a decrease in the adsorption capacity with Cr(III) at pH values above 6, due to the presence of Cr(OH)₄⁻ species at these pH values.

The amount of metal ions adsorbed was further investigated using static regime. As shown in Tables 2 and 3, a higher adsorption capacity was found with the static mode than that with dynamic mode. According to these results metal ions adsorbed at pH 5 using static regime was 11–40% higher than that with dynamic mode. The difference between adsorption capacities, found by static and dynamic regime experiments, could be attributed to

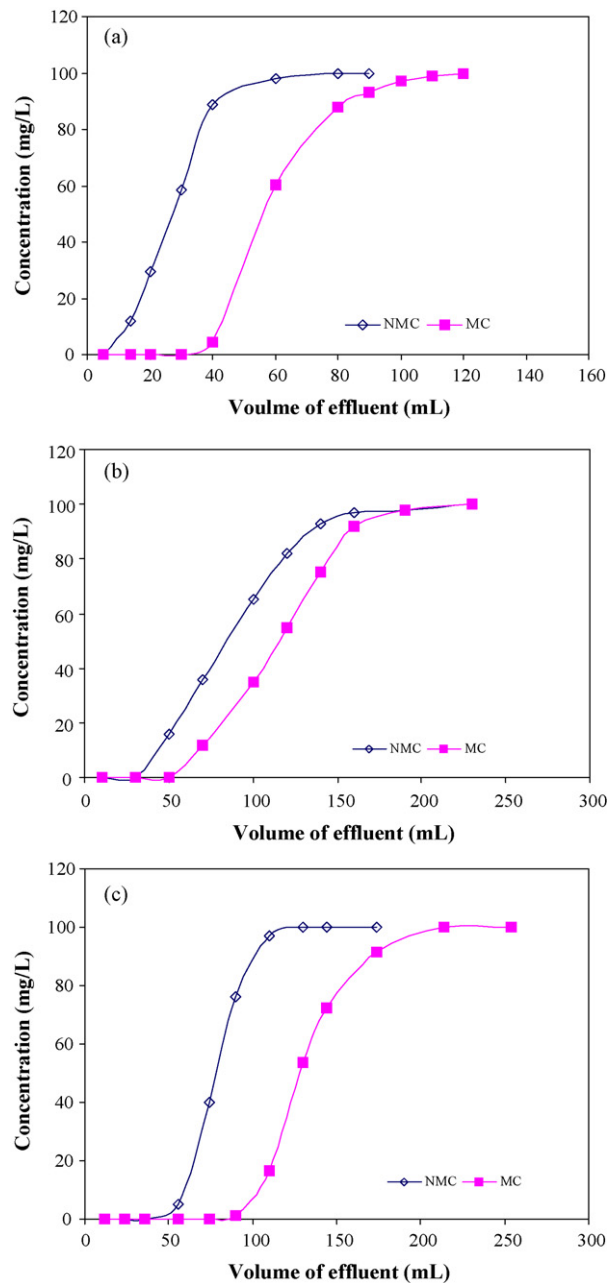


Fig. 6. Breakthrough curves of plain and tartrazine-modified carbon for Cd removal at different pH values. (a) pH 2; (b) pH 5; (c) pH 8. Conditions similar to Fig. 5.

the applied flow rate and, as a consequence, contact time was not sufficient to reach equilibrium and to have complete removal of metal ions.

In investigating the loading of tartrazine which was used for metal adsorption in the static mode at pH 5.0, it was found that

Table 2

Influence of the solution pH on the removal of Pb(II), Cd(II) and Cr(III) ions on plain and modified carbon in a static regime

pH	Pb (mg g ⁻¹)		Cd (mg g ⁻¹)		Cr (mg g ⁻¹)	
	NMC	MC	NMC	MC	NMC	MC
2.0	3.6	11.6	2.8	6.6	8.1	10.7
5.0	14.4	26.5	9.5	13.1	12.3	19.8
8.0	20.2	32.1	10.8	14.3	10.8	16.7

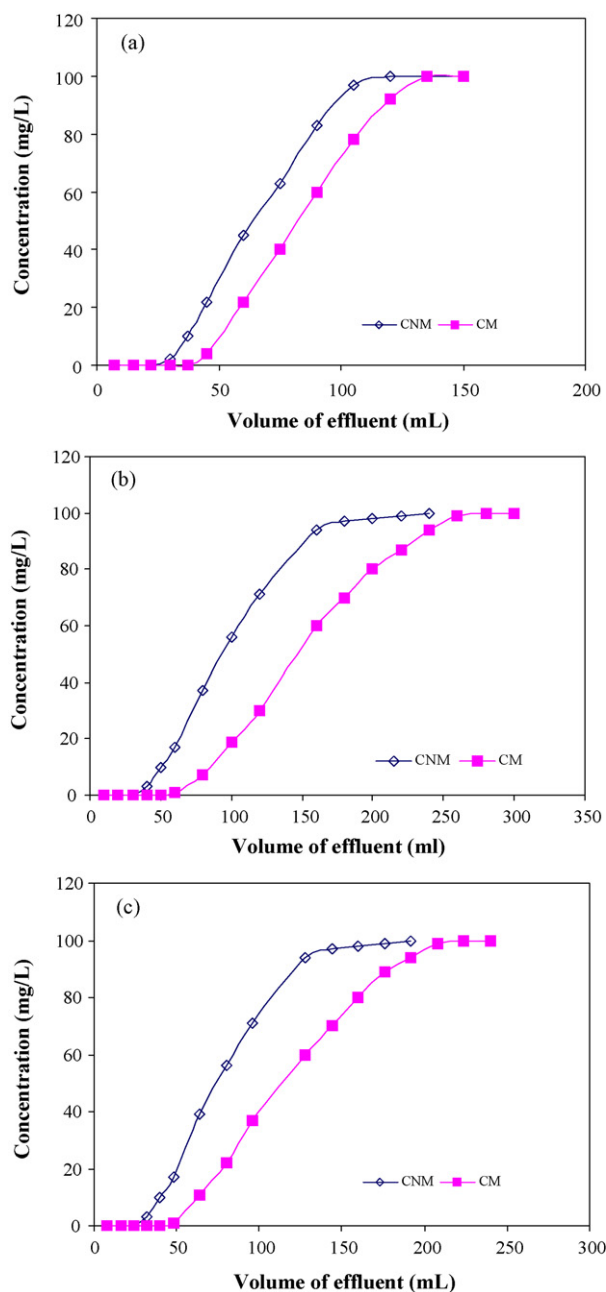


Fig. 7. Breakthrough curves of plain and tartrazine-modified carbon for Cr(III) removal at different pH values. (a) pH 2; (b) pH 5; (c) pH 8. Conditions similar to Fig. 5.

75 mg of tartrazine loaded could eliminate ~12 mg of Pb, 3.5 mg of Cd and 7.5 mg of Cr. These results indicate that 1 mol of tartrazine could eliminate 0.5 mole of Pb, 0.45 mol of Cd and 0.48 mol of Cr.

In an attempt to explore the efficacy of modified carbon column for the removal of metal ions in real samples, a synthetic water

Table 3
Influence of the solution pH on the removal of Pb(II), Cd(II) and Cr(III) ions on plain (NMC) and modified carbon (MC) in a dynamic regime

pH	Pb (mg g ⁻¹)		Cd (mg g ⁻¹)		Cr (mg g ⁻¹)	
	NMC	MC	NMC	MC	NMC	MC
2.0	3.0	7.2	2.5	6.0	7.1	9.1
5.0	12.3	19.5	8.8	12.0	10.6	16.9
8.0	14.0	25.5	9.2	13.2	8.6	13.3

Table 4

Analysis of a standard and synthetic water containing a mixture of Cd, Pb and Cr(III)

	STD solution		Synthetic water	
	CM	CNM	CM	CNM
Cr (mg g ⁻¹)	13.8	9.6	13.2	9.1
Cd (mg g ⁻¹)	11.2	7.8	9.5	7.2
Pb (mg g ⁻¹)	19.3	11.1	16.3	10.3

containing all three metal ions at a concentration level of 50 ppm each (pH of 5.0) was introduced into the column. It was found that the adsorption capacity of Pb, Cr and Cd (Table 4) was lower than that obtained with standard solutions of single metal ions which indicates the presence of competitive effect. With regards to the competitive effects, the column used confirms its efficacy for the removal of metal ions from industrial wastewater such as that of electroplating wastes. Furthermore, this technique could be used in a larger scale by using stainless steel columns packed with modified carbon and to compensate the high back pressure, pumps could be used to allow adequate flow rates.

Furthermore, the used column could be regenerated (desorption of tartrazine) using alkaline solution (0.5 M NaOH) containing ~10% ethanol. Rapid regeneration could be achieved using higher concentration of NaOH and ethanol.

4. Conclusion

The influence on the rate of adsorption of various factors, such as amount of tartrazine and pH of the system, have been investigated. Adsorption data fit well into the Langmuir adsorption isotherm, indicating formation of a monolayer over a homogeneous adsorbent surface. The adsorption of tartrazine onto activated carbon was found to follow a second-order kinetic model. The solution pH is one of the parameters with greatest influence on the adsorption of metal ions and tartrazine on activated carbon. This is because the charge of both the carbon surface and the adsorptive species depends on this parameter. Adsorption of tartrazine was maximum at pH below 5 and for metal ions it was maximum at pH greater than 5. The breakthrough values of carbon columns indicate that the purification efficacy of activated carbon was improved by the presence of tartrazine.

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