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PREPARATION OF ORANGE PEELS BY INSTANT CONTROLLED PRESSURE DROP AND CHEMICAL MODIFICATION FOR ITS USE AS BIOSORBENT OF ORGANIC POLLUTANTS

PREPARACIÓN DE CÁSCARAS DE NARANJA MEDIANTE DESCOMPRESIÓN INSTANTÁNEA CONTROLADA Y POSTERIOR MODIFICACIÓN QUÍMICA PARA USO COMO BIOSORBENTE DE CONTAMINANTES ORGÁNICOS

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Abstract

Some types of inactive biomass have been studied in terms of their adsorption properties as alternatives to the commonly used Activated Carbon (AC) such as orange peel. The present study evaluates a physical-chemical treatment for enhancing the adsorption capacity of raw orange peel for two model organic pollutants (azo dye and phenol). Instant Controlled Pressure Drop ("DIC" by its abbreviations in french), a vacuum drying technology, was applied as a first treatment, prior to chemical surface modification - either basic, using NaOH or acid, using Citric acid-. The use of DIC modifies and improves the structural properties of the material. Consequently, the combination of this technique followed by a chemical treatment shows an enhancement in the adsorption capacity of orange peels. The results showed that R-OH, R-COOH and R-COOCH$_3$ groups were present on the orange peel surface according to the treatment used. DIC treatment increases the adsorption capacity of raw orange peels 285% for the azo dye and 632% for phenol; DIC treatment plus adding the chemical surface modification, increase the adsorption 640% and 1812% for azo dye and phenol, accordingly. The present research work shows a novel technique for orange peels preparation as an adsorbent material.

Keywords: agroindustrial wastes, orange peels, biosorption, instant controlled pressure drop (DIC), wastewater treatment.

Resumen

Varios tipos de biomasas inactivas han sido estudiadas como material para preparar biosorbentes, un ejemplo son las cáscaras de naranja. El presente estudio evaluó un tratamiento físico y posterior modificación química para incrementar la capacidad de adsorción de cáscaras de naranja para dos compuestos orgánicos modelo (colorante-azo y fenol). Se empleó Descompresión Instantánea Controlada (DIC), una tecnología de secado combinada con descompresión al vacío como primer tratamiento; posteriormente se realizó una modificación empleando NaOH y ácido cítrico. El uso de DIC modifica la estructura del material, incrementando su porosidad y por tanto su área específica. La combinación de esta técnica con una modificación química posterior incrementa la capacidad de adsorción del material. Los resultados muestran la presencia de grupos R-OH, R-COOH y R-COOCH$_3$ en las cáscaras los cuales pueden incrementarse y modificarse con la preparación. El tratamiento DIC incrementa la capacidad de adsorción de las cáscaras en el orden de 2.1 para el colorante-azo y 7.32 para fenol. Mientras que la modificación química posterior al DIC incrementa la capacidad de adsorción en el orden de 3.65 y 19.12 para colorante-azo y fenol respectivamente. El presente estudio muestra una técnica novedosa para preparación de biosorbentes a partir de cáscaras de naranja.

Palabras clave: residuos agroindustriales, biosorción, descompresión instantánea controlada (DIC), preparación de biosorbente, tratamiento de aguas residuales.

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1 Introduction

Adsorption techniques have been applied because of their high removal efficiency of stable wastewater pollutants compared to other conventional methods. These processes allow achieving high quality effluents and are economically viable. Nowadays, it has been demonstrated the possibility of using former-considered waste materials or byproducts, as adsorbent resources represent alternatives to activated carbon. There are several studies related to the properties that different inactive biomasses possess for accumulating pollutants. While these materials are considered wastes with low or no economic value, and usually present removal and disposal problems, their transformation toward adsorbent materials add an economic value, and also help to reduce disposal costs (Crini, 2006).

One example of inert biomass is orange peel. This material is considered waste in the food industry, for instance, considering that in the preparation of an orange drink only the pulp is used and the rest of the fruit is discarded (Chatterjee *et al*., 2015) is evident that these residues have problems for disposal due to the large volumes they represent. However, these residues contain functional surface groups that are capable to bind contaminants. It has been observed that the properties of this material can be modified by a physical, chemical or physical-chemical previous treatment. Thereby, it is possible to accomplish higher adsorption capacities compared with untreated materials (Crini, 2005; Sha *et al*., 2009). Recently studies on orange peel preparation methods for adsorption processes are mainly based on chemical treatments, employing different acids and bases (Feng *et al*., 2009; Lu *et al*., 2009; Sha *et al*., 2009) these studies have been focused on the removal of metal ions as Cu(II) and Cd(II) from wastewater. Moreover, the use of a previous physical treatment in addition to chemical modifications could increase the adsorption capacity of the raw material.

For this purpose, Instant Controlled Pressure Drop (DIC) can be employed as a preparation process for biosorbents, since it is a vacuum-drying technology, commonly used for fruits and vegetables. By means of this technique, the raw peel is exposed to compression-decompression cycles, generally from 3 bars to vacuum (30 mbar). This process consists in the sudden evaporation of the inner water, allowing the material to expand, breaking cell walls and modifying the micro- and macro structure or the particles (Kamal *et al*., 2008). On the other hand, the material treated by DIC increases its porosity, the specific surface area and induces a microbiological decontamination (Setyopratomo *et al*., 2009). This technology has been successfully applied in food processing for the texturization of vegetable products (Louka and Allaf, 2004) as well as a pre-treatment in the extraction of essential oils (Besombes *et al*., 2010). Nowadays, employment of DIC process for the preparation of efficient biosorbents is a scarcely reported subject. In a previous study, we evaluated various parameters of operation of the DIC technology to study the preparation of biosorbents materials. It has been reported that this technology provides to the material adsorptive properties, such as increase in surface area and active sites available (Romero-Cano *et al*., 2016). Having obtained the operating parameters with it is possible to prepare these materials, it is necessary to evaluate the conditions and mechanisms by which it is performed adsorption of organic pollutants in aqueous solution, to project its use in wastewater treatment. Therefore, the reactive red dye 272 (RR-272- present in wastewater of the textile industry, and phenol-present in wastewater from pulp and paper bleaching facilities, resin, pesticide, insecticide, paint and solvent industries-were chosen as adsorbate model.

2 Materials and methods

2.1 *Preparation of orange peel for its use as biosorbent*

2.1.1 Untreated orange peels

Raw orange peels, abbreviated as OP, were obtained were collected from a food industry located in the city of Queretaro Mexico. Peels were washed with deionized water, and once their pulp was removed, were cut into pieces with an average size of 1-2 mm. These were later washed with a 20% ethanol solution (v/v) until the solution was clear and were then dried at 105 °C for 24 h in a conventional oven (Fig. 1a).

2.1.2 Biosorbents prepared from orange peels modified by DIC treatment

Instant Controlled Pressure Drop (DIC) was employed as a pretreatment in the preparation of orange peels for its use as biosorbent. This process involves a thermal treatment using steam injection in a chamber (”DIC reactor”). Orange peels were introduced into the DIC reactor operating at the following conditions: vacuum pressure of approximately 30 mbar, followed by 3 bar pressure by saturated steam for 90 seconds, afterward, an abrupt decompression to vacuum, and finally, injection of atmospheric air; the whole procedure is known as a DIC treatment cycle. This procedure was performed for 3 cycles (Romero-Cano y col., 2016). After this treatment, the material was washed and dried at 105°C. The final sample was labeled as OP-DIC (Fig. 1b).

2.1.3 Biosorbents prepared from orange peels modified by DIC treatment and with NaOH

20 g of OP-DIC sample was washed with a 20% ethanol solution for 24 hours at room temperature. Subsequently, it was filtered and rinsed with the ethanol solution until it remained clear. The material was then dried, placed in a flask and kept under stirring with a 0.1 M NaOH solution (10% w/v) for 1 hour at room temperature. Finally, the material was filtered and washed with distillated water until obtaining a clear solution (Lu *et al*. 2009), and dried at 105°C. The resulting sample was labeled as OP-DIC-Na. (Fig. 1c).

2.1.4 Biosorbents prepared from orange peels modified by DIC treatment and modification with NaOH and citric acid

5 g of sample OP-DIC-Na was added in a 100 ml of citric acid solution (0.6 M), and kept under stirring for 2 hours at 80°C. Afterward, it was filtered, rinsed with distillated water and dried at 105°C. This latter sample was labeled as OP-DIC-AC. (Fig. 1d).

2.2 Characterization of the prepared biosorbents

2.2.1 Surface chemistry characterization

The acid and basic sites of the prepared biosorbents were determined by Bohem acid-based titration methods (Boehm, 1994; Lu *et al*., 2009) using 0.2 g of biosorbent and 50 ml of neutralizing solution for 5 days. In order to determine the point of zero charge (pH_{pzc}) of the biosorbents, the following method was employed: the pH value of 50 mL 0.01M NaCl solution was adjusted between 2 and 12 (using either HCl 0.1 M or NaOH 0.1 M); afterward, 0.15 g of biosorbent was added and stirred for 48 h at room temperature. The pH_{pzc} was then calculated graphically according to (Faria *et al*., 2004).

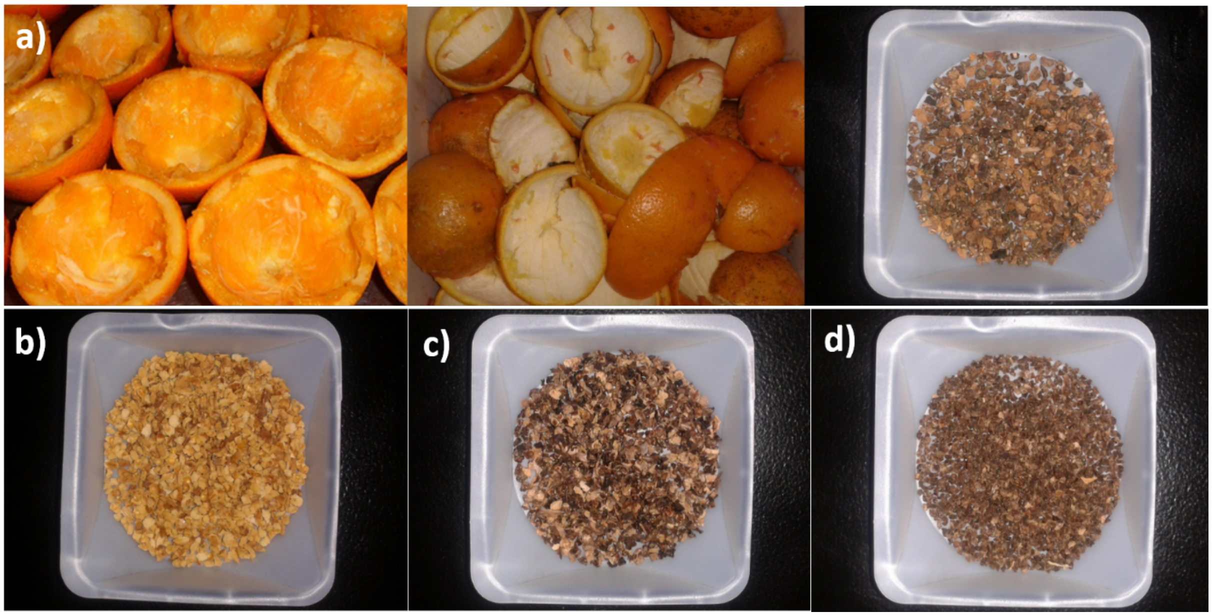

Fig. 1. Preparation of orange peel for its use as biosorbent.

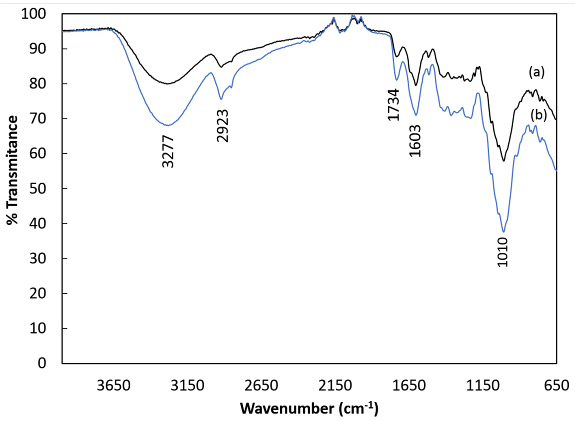

Fig. 2. FTIR spectra of: (a) Biosorbent OP, (b) Biosorbent OP-DIC.

2.2.2 Surface area

The specific surface area of biosorbents was measured by N_2 adsorption with a surface area analyzer Belcat Basic (BEL JAPAN INC.) using a single point method.

2.2.3 Scanning Electron Microscopy studies (SEM)

The prepared biosorbents were examined with a scanning electron microscopy. The micrographs were obtained using a SEM JEOL JSM-6610LV in SEI mode (Secondary Electron Imaging).

2.2.4 Infrared spectroscopy studies (FTIR)

Infrared spectra of the biosorbents were obtained using a Fourier Transform Infrared spectrophotometer Thermo-Nicolet, model Nexus equipped with a Specular Reflectance Module, in the range between 4000 and 400 cm^{-1} at an incident angle of 30°.

2.3 Adsorption experiments for organic compounds

In order to test the adsorption capacity of the prepared biosorbents, textile dye reactive red 272 (RR-272) and phenol were used as model compounds; solution of these compounds were prepared in distillated water for RR-272 and for phenol.

Phenol adsorption studies were performed at pH 7, so that phenol molecules were at their neutral form, pKa 9.89, thus favoring their adsorption. And the RR-272 adsorption studies were performed at pH 5, so RR-272 molecule was protonated by the sulphonated groups, pKa = 6.88, experimentally determined by potentiometric titration method described by (Wang *et al.*, 1998). All experiments were carried out with 1.5 gr of biosorbet, 200 mL of adsorbate, shaken at 180 rpm and T = 25°C. RR-272 (504.6 nm) and phenol (269.9 nm) concentration were evaluated using a UV-Vis GBC model Cintra 101 spectrophotometer.

The mass adsorbed (q_e) on the biosorbents was calculated by means of a mass balance for each experiment; the resulted data were analyzed by fitting to Langmuir and Freundlich isothermal adsorption models, which are presented in equation 1 and 2 correspondingly:

$$q_e = \frac{q_m K C_e}{1 + K C_e} \tag{1}$$

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

Where: q_e = adsorbed mass on equilibrium, mg/g biosorbent; K = Langmuir constant, L/mg; C_e = equilibrium concentration in solution, mg/L (ppm); q_m = maximum adsorption capacity, mg/g biosorbent; k_f = Freundlich constant (related to adsorption capacity); 1/n = adsorption intensity.

3 Results and discussion

3.1 Chemical characterization of the surface of the prepared orange peels

The experimental results about the biosorbents characterization of surface area, active sites and point of zero charge shown in Table 1. The surface area of OP-DIC increases in an order of 1.25 with respect to the peels without treatment (OP = 0.52 m^2/g vs OP-DIC = 0.65 m^2/g), also, the amount of active sites increased by 2.03 times, so that the DIC provides adsorbents properties. This effect is due to the DIC treatment causes the cell walls or the orange peels to collapse, which modifies its micro and macro structure and results in a more porous structure (Romero-Cano *et al.*, 2016), therefore, the surface area and the number of active sites increases, as they become more accessible. From Infrared spectra (Fig. 2), a significant increase in peak intensity for the OP-DIC biosorbent compared to the OP sample can be distinguished. This effect may be due to DIC treatment, which promotes a greater number of R-OH, R-COOH and R-$COOCH_3$ free groups on the biosorbent surface. These support the results obtained during the determination of active sites.

Table 1. Characterization of the prepared biosorbents: surface area, active sites and point of zero charge (pH_{pzc})

Biosorbents	Surface area (m^2/g)	Acidic sites (mmol/g)	Basic sites (mmol/g)	Total active sites (mmol/g)	pH_{pzc}
OP	0.52	3.12	0.69	3.81	4.5
OP-DIC	0.65	4.94	2.80	7.74	6.0
OP-DIC-Na	0.44	3.33	4.80	8.13	7.5
OP-DIC-Ac	0.18	6.50	0.08	6.58	3.2

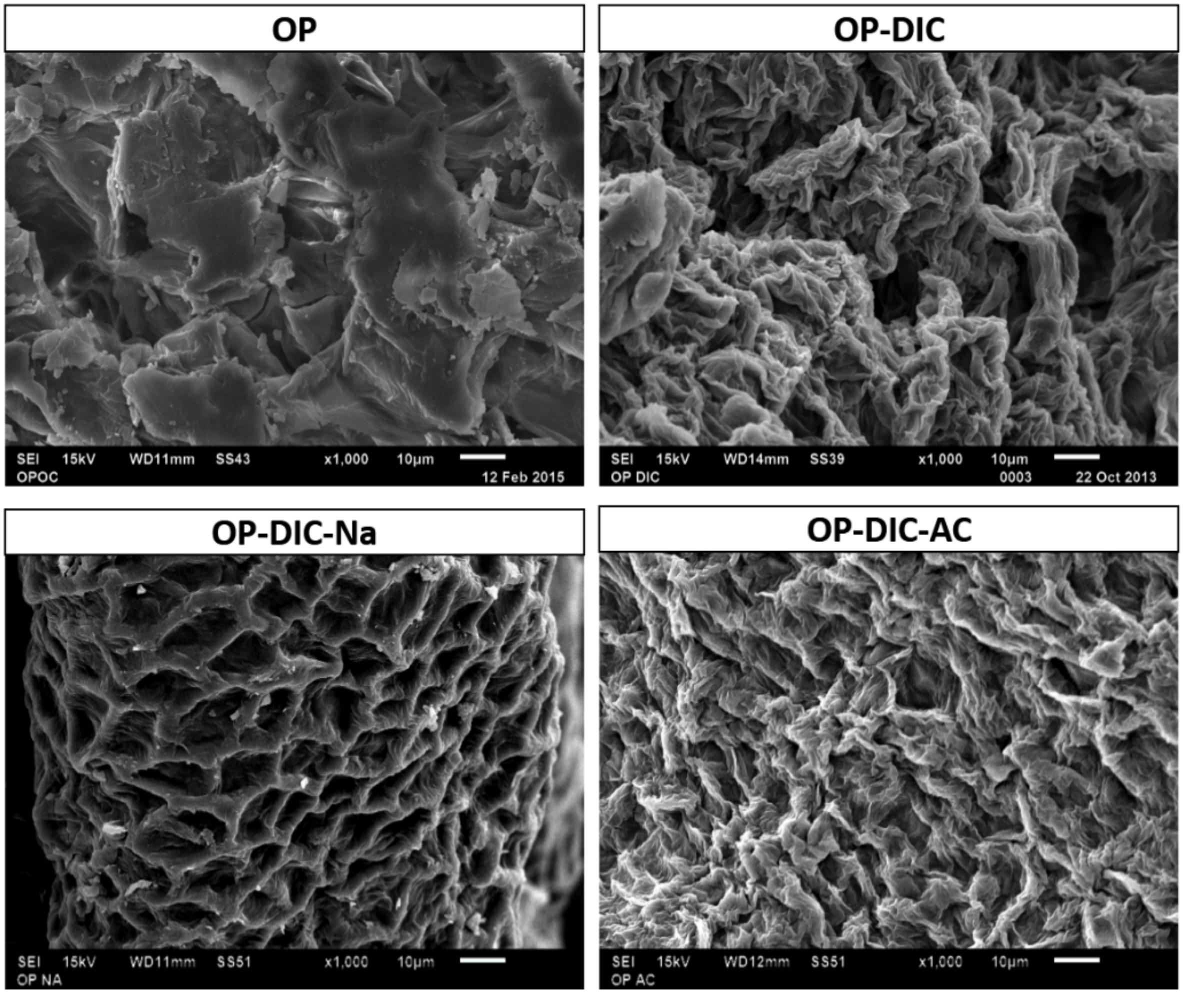

Fig. 3. SEM images for orange peels: OP (original orange peel); OP-DIC (after DIC process); OP-DIC-Na (after treatment with NaOH); OP-DIC-AC (after treatment with NaOH and citric acid).

After chemical modifications, the surface area of the material is reduced (OP-DIC-Na = 0.44 m^2/g and OP-DIC-AC = 0.18 m^2/g). Nevertheless, the swelling of peels during the treatment increases their porosity, and thus, modifies their physical structure; as a result, diffusion of species and mass transfer for the chemical modification and for the adsorption process is improved (Kamal *et al.*, 2012). In addition, chemical cleansing and further treatment allows extraction of other compounds and small organic molecules present on the biosorbent surface, which generates more active sites available.

The chemical treatments increase hidroxyl and carboxyl groups on the surface of the biosorbents; also, it was noticed that the concentration of the basic sites decreases as the number of acid sites increases, and vice versa, indicating the coexistence of both groups on the biosorbent surface and that they can be modified regarding the chemical treatment employed. This surface chemical modification was verified by the FTIR studies of the surface. In addition, the pH_{pzc} of the biosorbents varies according to the concentration of acid site and basic sites.

3.2 *Scanning Electron Microscopy (SEM) studies*

Micrographs were obtained using a 1000X magnification. As shown in Figure 3, the surface of the OP biosorbent presents well-structured layers without a well-defined direction; also, cavities and channels - typical features of macroporous materials - can be observed. When comparing OP-DIC biosorbent images to those of OP, DIC treatment is evidenced by slight structural alterations. Although OP-DIC micrographs show a similar morphology as the sample prepared by conventional washing and drying, the former acquire a porous and more irregular surface. Furthermore, it can be concluded that the biosorbent preparation by DIC technology does not cause destruction or severe attack to the biomass; this effect results from the conservation of the original structure of the peel, which is favorable during the biosorbents conditioning.

The biosorbents prepared after subsequent chemical treatments present a considerable change in their morphology as their structure become much more irregular; also, a uniform distribution of pores was achieved as shown OP-DIC-Na. From the observations above presented, these biosorbents have a higher surface area, which results in an enhancement in their adsorption capacity.

3.3 *Infrared Spectroscopy (FTIR) studies*

The FTIR spectra of the biosorbents prepared with chemical treatment are shown in Figure 4 and 5; in contrast with the spectrum of the pre-treated sample OP-DIC, the chemical modifications on the raw material through the different treatment processes can be observed. In the case of OP-DIC-Na sample (Fig 4a), it is proposed that demethylation of $-COOCH_3$ groups existing in pectin and lignin on the orange peel takes place, and hence, the amount of carboxylate ions is increased ($-COO^-$) (Feng *et al.*, 2010). OP-DIC sample shows well-defined peaks at 1365 and 1734 cm^{-1} - expected of C=O stretching vibrations - are

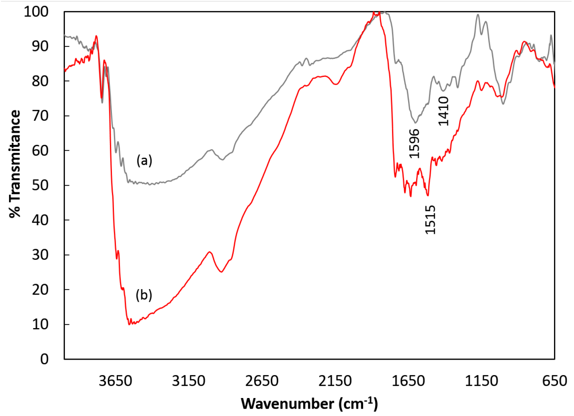

Fig. 4. FTIR spectrum of: (a) Biosorbent OP-DIC-Na (b) Biosorbent OP-DIC-Na after RR-272 dye adsorption.

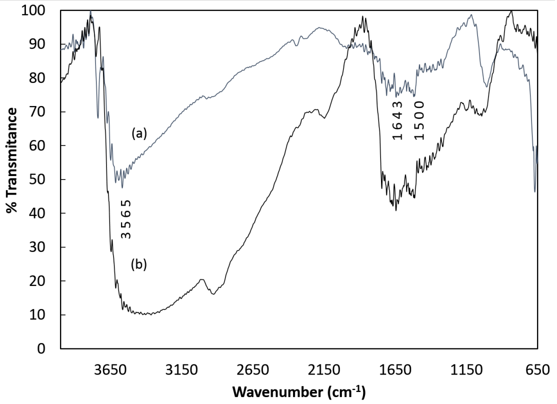

Fig. 5. FTIR spectrum of: (a) Biosorbent OP-DIC.AC, (b) Biosorbent OP-DIC-AC after phenol adsorption.

associated to non-ionic carboxylic groups ($-COOH$, $-COOCH_3$) (Kamal *et al.*, 2012) after treatment with NaOH, these signals decrease in intensity. Such behavior can be verified when comparing to OP-DIC-Na spectrum, in which two new signals were observed at 1575 and 1410 cm^{-1}; these peaks are attributed to vibrations of symmetric and asymmetric stretching of ionic carboxylic groups ($-COO^-$) (Feng *et al.*, 2010). In the case of OP-DIC-AC (Fig. 5a), it is suggested that a surface chemical modification occurs during heating with citric acid. This process allows the formation of citric acid anhydride as a condensation product, which also combines with hydroxyl groups of cellulose and hemicellulose forming an ester bond, and thus, the amount of carboxyl groups on the surface increases (Li *et al.*, 2007). These modifications can be observed in OP-DIC-AC spectrum (Figure 5a), in which new signals were found in the range of 1500-1800 cm^{-1}, being the most important those that were detected at 1643, 1665, 1684, 1711, 1726 and 1745

cm^{-1}. In addition, a difference in intensity of the OH region was noticed; this can be related to molecular interactions of COOH groups (Gusev & Ermolenko, 1965).

3.4 Adsorption studies

Experimental data of the adsorption batch test at equilibrium were analyzed on both Langmuir and Freundlich models (Table 2). As shown in Figs. 6 and 7, adsorption isotherms for RR-272 and phenol were fitted to the Langmuir model. This result suggests that these pollutants are adsorbed as a monolayer on the biosorbent surface, which agrees with other studies for the adsorption of different dyes using raw orange (Annadurai *et al.*, 2002).

3.4.1 Reactive red dye 272 adsorption

Biosorbents have higher adsorption capacities (larger q_{max} value) for the dye RR-272 in the following order:

$$OP-DIC-Na > OP-DIC > OP-DIC-AC > OP$$

Using DIC pre-treatment (OP-DIC), the adsorption capacity was 284% higher than the raw orange peel (sample OP) prepared by simple washing and drying. Furthermore, when using an additional chemical treatment with NaOH (sample OP-DIC-Na), adsorption capacity increased 639%.

At pH 5, samples OP-DIC and OP-DIC-Na revealed a positive surface charge, since their $pH_{pzc} > pH\ 5$. For samples OP and OP-DIC-AC an opposite behavior was found ($pH_{pzc} < pH\ 5$) (Faria *et al.*, 2004). If adsorption of dye RR-272 occurred only by a physical sorption process, then an opposite behavior for the adsorption capacity than that observed in the experimental data would have been found. This is explained because the RR-272 molecule is protonated by the sulphonated groups (pKa = 6.88) at pH 5 therefore it is prone to be adsorbed on surfaces with negative charge. In addition, using the Freundlich model for adsorption analysis, the highest value of 1/n was achieved for the sample OP-DIC-Na (Table 2), indicating the best adsorption capacity for this biosorbent; this observation confirms that a chemical sorption process for dye RR-272 on the biosorbents prepared occurs.

As a result, it is proposed that dye adsorption on the orange peel surface occurs via chemical sorption phenomenon, in a similar way to the dyeing process of cellulosic materials, in which covalent bonds between the dye reactive group and a cellulosate anion are formed (Karapinar *et al.*, 2007). This is evidenced by the OP-DIC-Na FTIR spectrum (Fig. 4b), where a new band appeared at 1515 cm^{-1}, and may be associated to azo bonds from the attached dye to the biosorbent surface (Maradiya, 2010). Moreover, the band close to 1500-1600 cm^{-1} disappeared, suggesting the presence of C=O groups from carboxylate ion during the adsorption reaction.

3.4.2 Phenol adsorption

The adsorption capacity of biosorbents was dependent on the type of treatment, showing higher values in the following order:

$$OP-DIC-AC > OP-DIC > OP-DIC-Na > OP$$

Table 2. Langmuir and Freundlich parameters for the adsorption of RR-272 (pH 5) and phenol (pH 7) on raw orange peel and chemically modified biosorbents

Biosorbent	Adsorbate	Langmuir				Freundlich			
		q_m (mg/g)	K (L/mg)	R	Standard Error	k_f	1/n	R	Standard Error
OP	RR-272	4.63	0.0020	0.995	0.091	0.035	0.6753	0.989	0.144
	Phenol	2.08	0.0089	0.994	0.077	0.166	0.4394	0.998	0.038
OP-DIC	RR-272	17.83	0.0005	0.996	0.125	0.022	0.8327	0.995	0.141
	Phenol	15.23	0.0010	0.990	0.631	0.769	0.3153	0.949	1.461
OP-DIC-Na	RR-272	34.27	0.0004	0.997	0.208	0.028	0.8704	0.995	0.265
	Phenol	12.15	0.0004	0.985	0.622	0.328	0.3626	0.954	1.082
OP-DIC-Ac	RR-272	14.92	0.0007	0.998	0.093	0.0233	0.8218	0.996	0.119
	Phenol	39.77	0.0006	0.991	1.562	1.300	0.3628	0.960	3.406

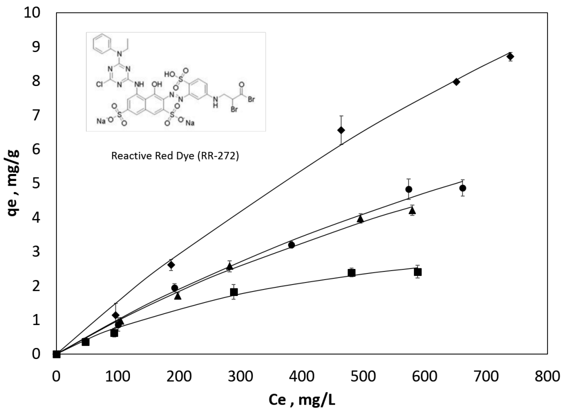

Fig. 6. Adsorption isotherms of RR-272 onto biosorbents prepared from orange peels. T=25°C, pH 5.

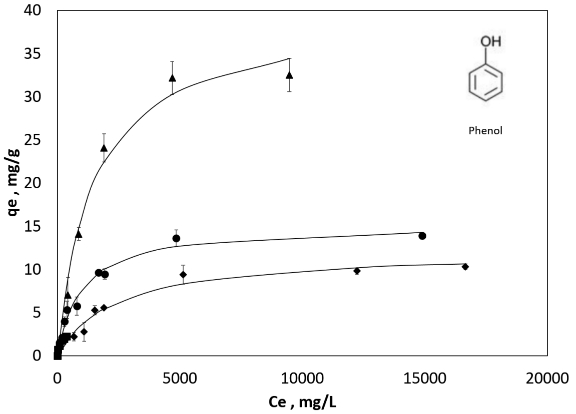

Fig. 7. Adsorption isotherms of phenol onto biosorbents prepared from orange peels. T=25°C, pH 7.

The DIC pre-treatment (OP-DIC) exhibited an increase in the adsorption capacity of 632% higher than OP. In addition, adsorption capacity increases 1812% when the material was prepared with citric acid (OP-DIC-AC), and in contrast, 484% with the NaOH treatment (OP-DIC-Na).

OP-DIC and OP-DIC-AC biosorbents have higher adsorption capacities for phenol, which is attributed to the negative surface charge, due to their $pH_{pzc} < pH$ (pH 7). At these pH conditions, the phenol molecule was protonated (pKa = 9.89), and consequently, physical sorption phenomena became predominant. Besides, OP-DIC-AC presented a higher adsorption capacity than OP-DIC for phenol; this effect is due to the acid citric treatment, which modifies the hydroxyl groups of cellulose and hemicellulose in orange peel. This effect increases the amount of carboxylic groups on the biosorbent surface, so that, the mechanism of adsorption is due to the presence of acid sites that interact with phenol in solution.

Phenol adsorption is likely to occur due to the formation of hydrogen bonds between the phenolic -OH and the acid sites available (R-COOH, R-OH), which are deprotonated at pH 7. This effect effect can be seen in the spectrum of sample OP-DIC-AC loaded with phenol (Fig. 5b), in which bands near to 3600 cm^{-1} were shifted to lower wavelength numbers due to the presence of hydrogen bridge bonds (Jung *et al.*, 2001). This assumption can be verified by observing a band shifting from 1010 cm^{-1} to a higher frequency, indicating that the oxygen of carboxylic groups contributed to the adsorption process (Kumar and Min, 2011). It was expected that the increase in the adsorption capacity was proportional to the change in the amount of available acid sites, however, the experimentally obtained increases are higher than these proportions. From this observation, it can be concluded that the adsorption of phenol on these biosorbents can also include other mechanisms. For instance, the first monolayer of adsorbed phenol molecules can interact with other phenol molecules in solution via $\pi - \pi$ interactions (Romero-Cano *et al.*, 2016).

A comparison of the adsorption capacities of phenol on different adsorbent surfaces prepared from natural materials and agro-industrial wastes is presented in Table 3. Orange peels prepared in this study presented comparable adsorption capacities and even higher than other natural materials (39.77 mg/g); the adsorbent material that had the best capacity for phenol removal from water were prepared by carbonizing, as in the case of the coir pith (48.31 mg/g). Nevertheless, the modification of orange peels for its use as adsorbent material by DIC process followed by chemical treatment is a competitive alternative compared to traditional methods such as carbonization of biomass.

Conclusions

Orange peel is an agroindustrial waste that can be used as a biosorbent material. Physical drying treatment by DIC induces changes in the peels surface and in the micro- and macro-structures by swelling, thus increasing their adsorption capacity. Modifications in the microstructure let an increase in surface area; therefore, DIC process enhances the subsequent chemical modifications due to a better mass transfer of the chemical solutions in the modified structure. Chemical treatment with NaOH and NaOH + citric

Table 3. Phenol adsorption on natural materials and agro-industrial wastes

Sorbents	Sorption capacity (mg/g)	Reference
Coir pith carbon	48.31	Namasivayam & Kavitha, (2006)
Residual coal	45.45	Ahmaruzzaman & Sharma, (2005)
Orange peel with DIC and NaOH -Citric acid treatment	39.77	Present study
Natural zeolites	32.6	Yousef *et al.* (2011)
Bentonite and kaolinite	25.57	Alkaram *et al.* (2009)
Porus clay heterostructure	15.4	Arellano-Cárdenas *et al.* (2005)
Orange peel with DIC treatment	13.47	Present study
Coal	13.28	Ahmaruzzaman & Sharma (2005)
Orange peel with DIC and NaOH treatment	12.15	Present study
Natural Clay	11.09	Djebbar *et al.* (2012)
Lignite	10	Polat *et al.* (2006)
Rice husk char	7.91	Ahmaruzzaman & Sharma, (2005)
Rice husk	4.50	Ahmaruzzaman & Sharma, (2005)
Raw orange peel	2.08	Present study
Modified clarion clay	1.24	Kaleta, (2006)

acid, changed the chemical surface groups present in the peels and increased their porosity, thus improving the biosorbent adsorption capacity and selectivity for organic pollutants, as tested with dye and phenol.

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