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Effect of Calcination on Orange Peels Characteristics: Application of an Industrial Dye Adsorption

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The present work is mainly concerned with the effect of calcinations of orange peel on its characteristics toward the adsorption of an industrial dye which is methylene blue.

In fact the results showed an increase of the specific surface area from for 0.45 to 4.97m^2/g for the solid material taken as crude for a calcination at a temperature up to 550°C for 30 minutes.

Also the equilibrium pH value variations insinuated the reduction of carboxyl and phenol functional groups with the creation of basic functions.

The IR spectra showed a similar distribution of peaks identified for the material at calcined state for three temperatures (300, 400, 550°C) with a marked change in the stretching section (> 1500 cm^{-1}) comparatively with support in the original state.

The effect of temperature and duration of calcination showed that good adsorption capacity is obtained with a value of 9.74mg/g for an initial concentration of methylene blue of 100mg/l when using calcined orange peel at 400°C for two hours.

Linear regressions have shown that the kinetics is controlled by the pseudo second order model.

The isotherm for adsorption of methylene blue on calcined orange peel at different temperatures (300, 400, 550°C) for two hours was investigated. The experimental data are well interpreted by the Langmuir model and this for the three temperatures.

Keywords: Orange peels; methylene blue, calcination, adsorption.

1. Introduction

Discharge of colored wastewater from various industries such as those of food, paper, carpet, rubber, plastics, cosmetics, textile, etc., into natural streams has caused major problems, increasing the toxicity and COD (chemical oxygen demand) of the effluent, and also reducing the light penetration, with an impact on photosynthetic phenomena. Also the presence of dyes may cause allergic dermatitis, skin irritation, mutation, cancer, etc. In addition, biodegradation of some of them produce aromatic amines, which are highly carcinogenic (Azza et al., 2009). Recent studies indicated that approximately 12% of synthetic dyes are lost during manufacturing and processing operations, from which approximately 20% ended up into the industrial wastewaters (Ayhan, 2009). Treatment of dye-based effluents is considered as an important and also a challenging matter towards the environment, particularly with the more severe imposed regulations.

Various treatment methods including, physical, physico-chemical and chemical processes have been investigated for treating dye- bearing effluents (Essawy et al., 2008). All of these methods have different colour removal capabilities, capital costs and operating rates and among all of them, adsorption has been found to be more attractive to other techniques for wastewater treatment in terms of initial cost, simplicity of design and ease of operation and insensitivity of toxic substances. Activated carbon is the most widely used adsorbent with great success because of its high adsorption capacity, but its use is limited due to its high-cost, encouraging the search for cheaper substitutes. Natural materials that are available in large quantities may have potential as inexpensive sorbents (Nevine, 2009).

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Consequently, the objectives of this study are the determination of the influence of calcination of a biomaterial, namely orange peel on its surface properties as well as the different change for material induced by this activation.

2. Experimental

2.1 Preparation of adsorbent and slutions

Orange peel was collected locally. It was extensively washed under tap water to remove soil and dust, and then sprayed with distilled water. This biosorbent was cut into small pieces, dried in sunlight and in air oven at 100–105°C for 24 h. A part of this material was calcined at three different temperatures (300, 400, 550°C) in a furnace (HERAEUSd-6450 HANAU) during different times (30mins, 1hour and 2hours) at each temperature. The solid material was then crushed and sieved to recover the particles of about 0.315mm in diameter before its use as an adsorbent.

A stock solution of methylene blue (MB) with a concentration of 0.5g/l was prepared from the powder of the dye itself. The solutions to be tested were synthesized by successive dilutions of the stock solution to the desired concentrations. The pH of the solutions was adjusted with 0.1N HNO_3 (or 1N) and 0.1N NaOH (1N).

2.2 Characterization of raw and calcinated solids

The moisture content was calculated by weight difference before and after heating 5g of the sample at 105°C for 24 h. The ash content was estimated by calcination of the sample at 550°C in an oven of “Nabertherm Controller B180” type, for 2 hours. Calculation was carried out by differential weighing of the quantity of initial dry matter and that collected at the end of the calcination operation (Osnick, 2009).

For the determination of the equilibrium pH (pH_{equi}), a mass of 1g of solid was shaken in a glass flask with 100mL of distilled water ($pH = 5.2 \pm 0.2$) at 300 rpm for 24 h, pH measurement was carried out every 25mins, and finally after 24 hours.

The methylene blue method (Afnor norm 1992) was used for the determination of specific surface area of the materials. A mass of 500mg of sample finely crushed was shaken continuously in a glass flask with 10mL of distilled water to make a suspension for a few minutes. Then it was titrated by a solution of methylene blue 1g/L (drop by drop), the dosage was continued until the persistence of clear blue aureole surrounding the central repository of the formed spot on the paper.

The basics and acidic groups were determined with a procedure where a mass of 100 mg of sample was shaken in a glass flask with 50mL of 0.01 M of different basic and HCl solutions for 24 h. respectively, for the determination of acid and basic functions surface. The sample was filtrated and the excess of acid or base was titrated with 0.01M HCl or NaOH solutions. This method can also calculate the total acidity and alkalinity of an adsorbent material, leading to the sum of the respective acidic and basic functional groups. The result is expressed in mmol / g or meq / g of material.

A SHIMADZU FTIR 820 1PC spectroscopy apparatus was used to determine the presence of functional groups at room temperature in KBr pellets.

2.3 Test of the adsorption

The study of the adsorption of MB on the calcinated supports was based on the variation of the contact time to determine the kinetics of this process and the variation of the initial concentration of MB at the end to get the adequate isotherm model describing the results. The experimental procedure was conducted according to the steps below.(1) Preparation of a suspension supports-solution with a constant ratio S/L equal to 10 g/l; (2) The stirring was carried out at ambient temperature of 20 ± 2 ° C at 600 rpm;(3) 5 ml of suspension volume at various reaction times during 125 min was taking with a syringe and it was filtered with Millipore filter of 0.45μm diameter in all experiments;(4) Analysis of the filtrate was made using spectrophotometer a double beam UV–Vis spectrophotometer (UV- Shimadzu 160A) at 662 nm.

The equilibrium data were modelled using the Freundlich, Langmuir, and Temkin isotherm models.

The kinetics in most systems followed pseudo-first-order equation, pseudo second-order, or intra-particle diffusion.

3. Results and discussions

3.1 Physico-chemical characteristics

3.1.1Moisture and ash content

Table 1 shows physical characteristics of crude and calcinated oranges peels at different temperatures (300, 400, 550°C). From the results, the orange peel in the crude state (CrOP) showed a higher moisture content (5.247%) and volatile matter (97.014%) thus the rate of dry matter (94.75%) and ash (2.986%) less than that of peels in the calcined state. This can illustrate the effect of calcination treatment increasing the percentage of the dry matter from 94.75 to 99.3% and lowering the moisture content from 5.247 to 0.7%. Concerning natural orange peel, S. Kamsonlian et al. found the same result of ash content as that obtained in this work and which was 3.10 % (Kamsonlian et al., 2011).

Table 1: Volatile matter, ash content, dry matter and moisture of solids

Materials	*Volatile matter (%)*	*Ash content (%)*	*Dry Matter (%)*	*Moisture (%)*
COP 300°C	70.746	29.25	99.3	0.7
COP 400°C	92.365	7.635	97.1	2.9
COP 550°C	92.06	7.939	97.7	2.3
CrOP	97.014	2.986	94.75	5.25

3.1.2 Specific surface

The results presented in the Table 2 show that the calcination did significantly increase the surface area of the material (orange peel). At 300°C and 400°C, an increase in the duration of calcination caused a remarkable improvement of the specific surface area, which was not the case at 550°C where the relatively longer calcination time reduced the surface area from 4.9704 to 3.6148 m^2/g. this can be explained by the fact that at the thermal activation at 550°C and for a long time (2 hours), the material particles became so finer, reducing the porosity of the surface and hence compacting it to generate a lower surface area. This is confirmed in the literature where slightly different specific surface values of crude orange peel state are reported. For example Feng Ning- chuan et al. determined a value for the orange peel of 0.83 m^2/g using the BET method (Feng and Guo Xue-yi, 2010); whereas Kamsonlian et al. found a surface area of orange peels equal to1.856 m^2/g (Kamsonlian et al., 2011).

Table 2: Specific surface of various materials

Materials	*Specific surface (m^2/g)*	*Materials*	*Specific surface (m^2/g)*	*Materials*	*Specific surface (m^2/g)*
CrOP	*0.452*	*COP 400°C for 30min*	0.904	*COP 550°C for 1h*	4.518
COP 300°C for 30min	*1.130*	*COP 400°C for 1h*	1.807	*COP 550°C for2h*	3.615
COP 300°C for 1h	*3.163*	*COP 400°C for 2h*	2.259		
COP 300°C for 2h	*4.518*	*COP 550°C for 30min*	4.970		

3.1.3 The equilibrium pH

Table 3 summarizes the equilibrium pH measurements carried out on the suspensions of materials with distilled water during a contact time of 24 hours under an average agitation.

According to the results, the pH of crude orange peels (CrOP) was 4.648. So it is clear that the pH was acidic. Thereafter, an increase in pH was shown for the material after calcination, implying that the orange peel surface has an acidic character and the calcination changed it into basic. When increasing the calcination temperature the pH became clearly alkaline at 550°C and reached a value of 9.964.

Table 3: Equilibrium pH for each supports during 2 hours

Materials	*CrOP*	*COP 300°C*	*COP 400°C*	*COP 550°C*
pH	4.648	6.507	8.645	9.964

3.2 Surface chemistry

3.2.1 Determination of surface functions by Boehm's method

The determination of surface functions of the solid materials by Boehm's method gave the results shown in Table 4 where it can be found that the surface chemistry of the orange peel was affected by the calcination at 300°C and 400°C for different times. The heat treatment caused a reduction of the carboxyl and phenol groups, increasing the basic character of the surface. The calcination time extension induced a remarkable decrease in the content of phenol functions, resulting in an increase of the content of basic groups on the surface. These results confirm previous findings regarding the measurement of equilibrium pH.

Table 4: surfaces functions for the material at different state

Material	*Carboxyl Functions (mmol/g)*	*phenol Functions (mmol/g)*	*Total of acid functions*	*Basic functions (mmol/g)*
CrOP	2.457	3.842	6.299	2.59
COP 300°C for 30mins	2.38	1.322	3.702	2.757
COP 300°C for 1h	2.423	1.218	3.641	2.804
COP 300°C for 2h	2.363	1.15	3.513	2.815
COP 400°C for 30mins	2.246	1.242	3.488	3.80
COP 400°C for 1h	2.164	0.948	3.112	3.563

3.2.2 Analysis of the surface functions by infrared Fourier transforms spectroscopy

Figure 1 show that all spectra of the four supports present a broad band in the region 3521 - 3300 cm^{-1} which is assigned to the vibration of OH hydroxyl groups (carboxyl, alcohols or phenols) or related to amine groups (NH).

In the same region, a maximum of about 3400 cm^{-1} is observed in the spectrum of natural peels, confirming the presence of the hydroxyl functional groups. This band was slightly reduced when calcinating the solid at the three temperatures. A peak at 2931.6 cm^{-1} is observed in the spectrum of natural material which generally characterizes the vibration aliphatic CH. This peak is reduced for calcinated support (300 and 550°C) and undetectable for the calcinated solid at 400°C.

The weak peak at 1743.5cm^{-1} indicates the presence of C=O vibrations, which is attributed to C= O groups of carboxylic acids, acetate groups (COO^{-}), ketones, aldehydes and lactones (Jamil et al., 2008). For 1639cm^{-1}, this corresponds to an amine or NH amide bonds. This peak is slightly reduced in the case of calcination at 400 and 550°C, and disappeared totally on the spectrum of the calcinated support at 300°C.

The spectrum of natural orange peels also shows the different peaks in the spectral region between 1427.2 and 1064.6cm^{-1} due to vibrations of CO of ester, ether, carboxylic acid or alcohol. Similar peaks are observed by Khormaei et al. (Khormaei et al., 2007). Calcination reduces remarkably these peaks.

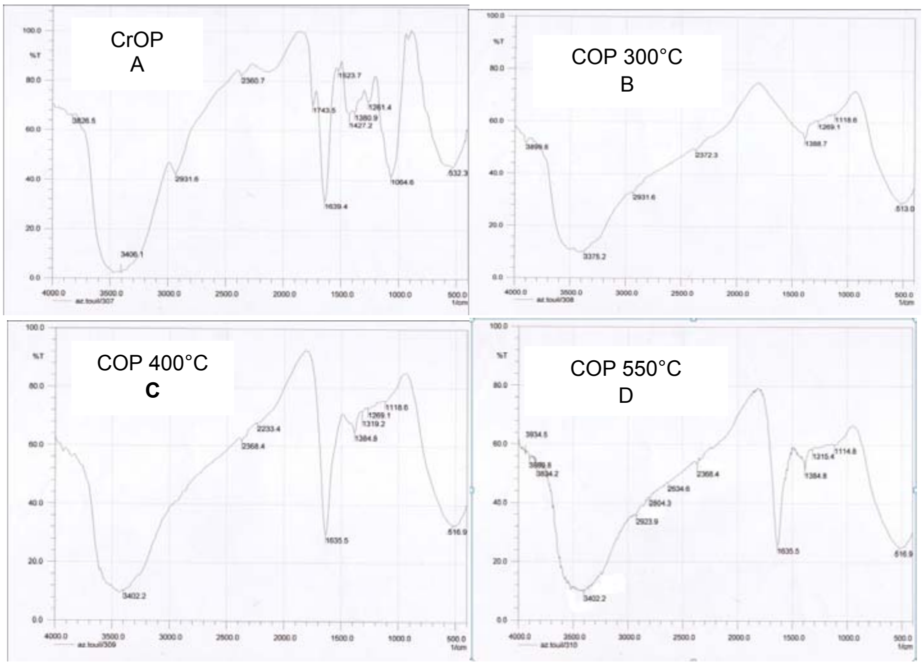

Figure 1: FTIR spectra of the ROP, COP300°C, COP400°C, and COP550°C (calcined for 2h)

3.3 Study of adsorption of MB by calcinated orange peel (COP)

3.3.1 Effect of calcination time

For the effect of calcination time, Figure 2 shows that at the temperature of 300°C, there was an increase in the adsorption capacity by increasing the time of the thermal activation from 30 minutes to 2 hours for a stirring time of 100 min. After this time the retention became identical and reached its limit value of 3.95mg/g. But this was not the case for the temperature 400°C where the curves of retention capacity were almost superposed with a slight variation, but they present maximum values of 3.89, 3.86 and 3.82mg/g for 30 min, 1h and 2h, respectively. At the calcination temperature of 550°C, the adsorption capacity was maximal at the activation time of 30 minutes and 1 hour, but for calcination of 2 hours, the BM retention became lower when a reduction in adsorption capacity was noticed. These results can be explained by the low porosity of calcinated peels at 300°C for 30 minutes, increasing in time of calcination to 1 and 2 hours, BM retention increases which means increasing number of vacant sites on the peel surface. This is justified by the results of the specific surface. The same observations were found in the case of calcination at 400°C. The organic nature of the material surface selected contained acidic and basic functional groups which promoted more the retention of MB which is a cationic dye; therefore chemical reactions will take place between the pollutant and the functions of the surface (chemisorption). At a temperature of 550°C for 2 hours, the organic material was converted to volatile matter and therefore leaving just the mineral material. Consequently the retention with surface functions was negligible and the adsorption may just be due to the diffusion mechanism through the pores of the surface.

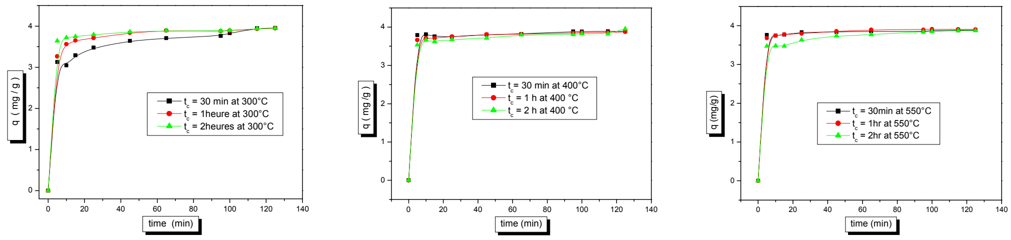

Figure 2: The effect of duration of calcinations on BM adsorption: C_0=40mg/L, pH=4.98

3.4 Adsorption kinetics

Adsorption kinetic describes the controlling mechanism of adsorption processes which in turn governs the mass transfer and equilibrium time (Mestre et al., 2011). The experimental data of MB adsorption onto calcinated orange peel (COP) at 300, 400, 550°C at different time intervals were examined using pseudo-first-order, pseudo second-order and intra-particle diffusion kinetic models, The corresponding results are shown in Table 5. Pseudo-second-order kinetic model gave the best fit, with highest correlation coefficients, suggesting that the overall rate of the adsorption process was controlled by chemisorption which involved valency forces through electrons sharing between the adsorbent and adsorbate and higher adsorption energy.

Table 5: Kinetic models parameters for the adsorption of MB onto COP at C_{0MB}=40mg/L

	Pseudo-first order		*Pseudo-second-order*		*Intra-particle diffusion*	
	k_1	R	k_2	R	k_{int}	R
300°C	0.023	-0.9189	1.182	0.9999	0.4396	0.8555
400°C	0.010	-0.9572	0.76	0.99965	0.3921	0.7176
550°C	0.1225	-0.7893	0.630	0.99993	0.3698	0.9564

3.5 Adsorption isotherms

Three theoretical models were tested on the experimental results, Langmuir, Freundlich and Temkin. The Langmuir isotherm assumes the formation of a monolayer of the adsorbent over a homogeneous surface adsorbent with all molecules having the same activation energy (Foo and Hameed, 2012). While the Freundlich isotherm assumes that the surface is heterogeneous with a non-uniform distribution of the heat of adsorption over the surface and where a multi-layer adsorption can be displayed. Temkin found that the heat of adsorption due to interactions with the adsorbate decreases linearly with the recovery rate. According linearization results it can be concluded that the retention mechanism of MB by calcinated orange peel is represented by the Langmuir model. Table 6 below gives all constants isotherms applied and their correlation factors which confirm the previous conclusion.

Table 6: Isotherm parameters for the adsorption of MB onto COP

	Langmuir			*Freundlich*			*Temkin*		
	q_{max}	K_L	*R*	K_f	*1/n*	*R*	K_T	B_T	*R*
300°C	14.308	0.601	0.988	4.761	0.538	0.962	8.015	2.645	0.979
400°C	14.845	0.780	0.999	6.043	0.634	0.989	8.609	3.110	0.995
550°C	7.304	1.196	0.997	3.155	0.258	0.898	27.22	1.052	0.944

4. Conclusion

The best results of this study, confirm that increasing of temperature of calcination induce an increase in the surface area but for a time less than 30min because heating during a long time may lead to a degradation of the organic matter contained in the biomaterial and reduce the specific surface. The experiments showed that crude orange peel (CrOP) had an acidic character and the calcination changed it into a basic one.

The effect of the temperature and calcination time show that the adsorption capacity was more pronounced with an initial concentration of the MB of 100mg/l, when using calcinated orange peels at 400°C for two hours.Thus, the organic nature of the selected material that contains basic functional groups favours more the retention of the MB which is a cationic dye.

By considering the experimental results and adsorption models applied in this study, it can be concluded that adsorption of MB obeys Langmuir isotherm. Adsorption kinetics follows pseudo-second order kinetic model. Kinetic results showed that both film and particle diffusion is effective adsorption mechanisms.

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