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Preliminary Study on Benzoic Acid Adsorption from Crude Active Coals and Bentonite

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Abstract - We studied the adsorption of pollutant benzoic acid by the modified bentonite of Maghnia (west of Algeria), and coal (Coal from the mines, southwest of Algeria, Bechar area) under three forms, crude and activated. Kinetic data show that the balance of bentonite (as amended) adsorbs organic acids better than activated and raw coal. Indeed, the intercalation of bentonite with benzoic acid causes an improvement in the texture of porous material, which allows its use in the adsorption of organic compounds. The adsorption isotherms (Langmuir and Freundlich) indicate that the adsorption of benzoic acid by the coal and bentonite yielded results favorably. The results obtained showed the practical value of using the activated coal and bentonite (as amended) in the field of remediation of water contaminated with organic pollutants.

Keywords: Bentonite; Coal; Adsorption; Benzoic acid; Kinetic

Introduction

Coal is a sedimentary rock of organic origin, which comes from the degradation of a wide variety of precursor's higher plants, ferns, algae, fungi, spores, etc. Land filling, progressive organic material causes their maturation, essentially by increasing the temperature parameter plus the pressure for embedded coals. This development led to Coalification called anthracite and is accompanied by considerable physical and chemical changes (Abbes *et al.*, 2010). The geologic age of the carbons is between 300 million years. The organic material is enriched with carbon initially losing water and carbon dioxide, and then the first liquid hydrocarbon and gas. The coal is mainly composed of carbon, hydrogen, oxygen and a little sulfur and nitrogen. Study of paleogeographic of different geological epochs of Algeria has shown that only the continental formations, the Carboniferous contain indices and deposits of coal having a certain value. In more recent formations of the Jurassic, Cretaceous and Tertiary lignite few clues. Northern Algeria Paleo-geography shows no conditions for the formation of coal. Adsorption techniques have been successful in removing organic species.

Currently, coal is the most commonly used adsorbent through its adsorbent power which is very important against the organic compounds, but the inconvenience is that coal is expensive in costs (Loison *et al.*, 1989) the preparation requires large investments (oxidation, grinding, pyrolysis, activation, packaging. In this context, that we proposed to test adsorbents competitive with coal-based clays available, in large quantities in our country, because of its easy and inexpensive operation. Clays are regarded today as being interesting adsorbent materials. Because of their low cost, abundance on all continents, their ion exchange properties and high surface area, the ability of clay minerals (BENTONITE, Montmorillonite) to adsorb organic molecules and / or mineral is a subject that has aroused great interest for many years (Akçay *et al.*, 2004; Bouras, 2003). The objective of the present work was to eliminate of phenol and benzoic acid by adsorption on a carbon raw coal and activated (Coal from the mine to the Bechar region and bentonite from the Region Maghnia). The development of such effective barriers, local resource base can help to partially

solve the problem of water contamination. The present work attempts to solve pollution problems in watery surroundings by aromatic compounds such as the phenol and the benzoic acid. Several ways of elimination of these compounds were the object of different (Bared *et al.*, 2010).

Materials and Methods

An Algerian Coal from the region of Bechar was used as the starting material. The characteristics of the adsorbent used are shown in Table 1 (Abbes *et al.*, 2010; Eren *et al.*, 2009). The coal comes from oxidized organic matter or coal fossilized wood. It is the densest maceral (density between 0.4 and 0.8), hard but friable, rich in carbon, hydrogen-poor and volatile matter The minerals are generally low proportion in coal are(Si,Fe,Ca,Al,Mg,K.Na,Al,B,Va,Ta) les Matières Minérales Sont constituées D'inclusions Minérales visibles à l'analyse microscopique. After burning coal, mineral materials are the ashes (Deul *et al.*, 1956).

Preparing raw coal and pyrolysis

The coal is crushed using an electric grinder (SM 100 Type RETSH) Then sifted through 03,502 pulverizes type and brand Fritsch, to be reduced to elementary particles with a diameter between 0.13 and 0.49 mm. These materials subjected to pyrolysis which consists of a thermal activation, calcination at 700 ° C by controlled thermal programming for 2h (Abbes *et al.*, 2010). To achieve pyrolysis equipment must be cleansed and arrow, then a sample of about 45g of 0.2 mm diameter coal is placed in a quartz reactor itself - same content in a horizontal furnace. A purge is carried out for 15 min with argon. One begins to heat at 1000ºC. The sample was heat-treated in an argon flow 80 cm3 / min. The heating rate was 50C / min. The permanence time at the final temperature is 30 minutes Yields ash coal were determined, (Graiyna, 1996).Initial mass of crude coal = 45g. , ash efficiency=0.8 %, coal efficiency=51 %. Final mass of Coal = 23g.Ash Mass = 0.36g.

Pyrolysis of a carbonaceous precursor, oxygen rich, low aromatic, is made to obtain a solid with high carbon content. The carbon enrichment is done by heat treatment under an inert atmosphere. During this process, we see an elimination of volatile materials: water (resulting from a reaction of hydration of alcohol groups) and carbon dioxide (decarboxylation product or decomposition lactones and anhydride), then monoxide atoms which share in general at a higher temperature beyond 550 °C (resulting from the decomposition of aldehydes and ketones), and finally liquid hydrocarbon (such as- tar) and volatile gaseous hydrocarbons.

Table1. Coal characteristics of the mines in the area of Bechar

Ultimate wt.%, dry ash-free basis		Proximate wt.%, as-received	
Hydrogen	4.2 - 4.7	Ash	5 -19
Nitrogen	1.6 - 1.9	Total sulfur	0,97- 5,3
Sulfur	1.2 - 4.2	Humidity	0,2 - 0,8
Oxygen	8.5 - 16.7	Volatile matter	12,0 -24,5
Inorganic Carbon	0.2	Fixed carbon	46 ,3 - 56
		Organic Carbon	75.8 - 81.2

Table 2. Analyzes results of trace elements in coal

Analysis elements	Percentage%	Analysis elements	Percentage%
Si	11.80 –14.70	Ni	0.04 – 0.06
Fe	12.50 – 17.30	Sn	0.01 – 0.03
Ca	12.70 – 20.50	Zn	0.03 – 0.06
Al	06.80 – 07.60	Li	0.01
Mg	01.40 – 02.10	Cu	0.02 – 0.05
K	01.20 – 01.60	Sr	0,01 – 0.06
Na	00.30 – 01.30	Cd	0.01 – 0.02
Mn	00.10 – 00.20	Cr	0.01 – 0.02
V	0.010 –00.05	Sb	0.01
Ba	0.070 – 00.09	Pb	0.01
Ti	0.040		

Chemical activation of coal by ZnCl2, NaOH, H$_3$PO$_4$

The activation role, removed all heavy hydrocarbons, tars type which remain fixed in the coal, and it also helps develop pores, thus increasing the surface of the active substance. The calcination removes volatile material in order to keep only the carbon skeleton. 2g coke mixed with a solution containing 10 cm^3 of water, and 4 g of active agent, for 2 hours every time the experiment was repeated with three active agents (H$_3$PO$_4$, ZnCl$_2$, and NaOH).The samples were dried at (110°C) for 24 hours in an oven. The dry mixtures were heat treated, is added a stream of argon (80 cm3/min) into a horizontal cylindrical oven .The heating rate of 50°C / min and the activation temperature of 700°C for 2H .The activated coal washed with HCl (5M), then with distilled water until chloride ion purificaton. Finally, the sample was dried at 1100°C for 12 h. Coal efficiency enabled by H$_3$PO$_4$> NaOH by activated coal efficiency> activated coal yield is ZnCl$_2$.NaOH by activated coal ash rate> coal ash rate activated by ZnCl$_2$> Ash content of coal activated by H$_3$PO$_4$.Phosphoric acid is the best activating agent because of the ash yield of the activated coal H3PO4 is 9%, which a very large value

Table 3. Output of the activated coal

Initial Mass 2g	Final Mass	Yields of coal	Ash Rate
Coal activated (ZnCl$_2$)	1.60	80 %	10 %
Coal activated (NaOH)	1.65	82 %	12%
Coal activated (H$_3$PO$_4$)	1.75	87%	9%

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Physico-chemical characterization of the modified bentonite Maghnia

The bentonite used in our work is extracted from Hammam-Boughrara at Maghnia (Tlemcen). Our finely ground was provided by the company ENOF bentonite of Maghnia (Tlemcen, Algeria). Bentonite is a mixture of montmorillonite, kaolin, and quartz and calcite impurities. The specific surface area is 55.186 m²/g. The pH is 9.48. The Table 4 and Table 5 showed the results of analysis of the chemical composition of the clay used. ENOF (National business nonferrous mining products).

Table 4. Bentonite chemical composition of Maghnia (Algeria)

Constituents	SiO$_2$	Al$_2$O$_3$	CaO	MgO	K$_2$O	Na$_2$O
Percentage (%)	59	16	3-6	2-4	1-2	2-4

Table 5. Physical properties of the montmorillonite Maghnia (Algeria)

Density related (kg m^{-3})	true density (kgm^{-3})	pH	Specific surface (m² g^{-1})	pore volume (ml g^{-1})	Fire loss (% mass)	Humidity (%)	Color
1200	2600	8.5	24	0.01	12	16	White

Results and Discussion
Spectrophotometer UV-visible, benzoic acid determination methods

Analyses are performed on a Shimadzu spectrophotometer 8543 model controlled by a computer. The highest wavelengths are obtained by automatic scanning between 200 and 800 nm. Quartz cell of (1 cm) optical path are used. Witness's solutions without adsorbents are prepared to ensure that there is no interference with time (Bouras, 2003).The benzoic acid assay is carried out in the UV with a wavelength of 271 nm corresponding to the maximum absorbance.

Table 6. Maximum wavelength of benzoic acid

λ_{max}	200	210	220	230	240	250	260	261	262	263	264	265	266	267
DO	0	0	0.03	0	0,039	0,036	0,051	0,047	0,097	0,142	0,177	0,23	0,219	0,282

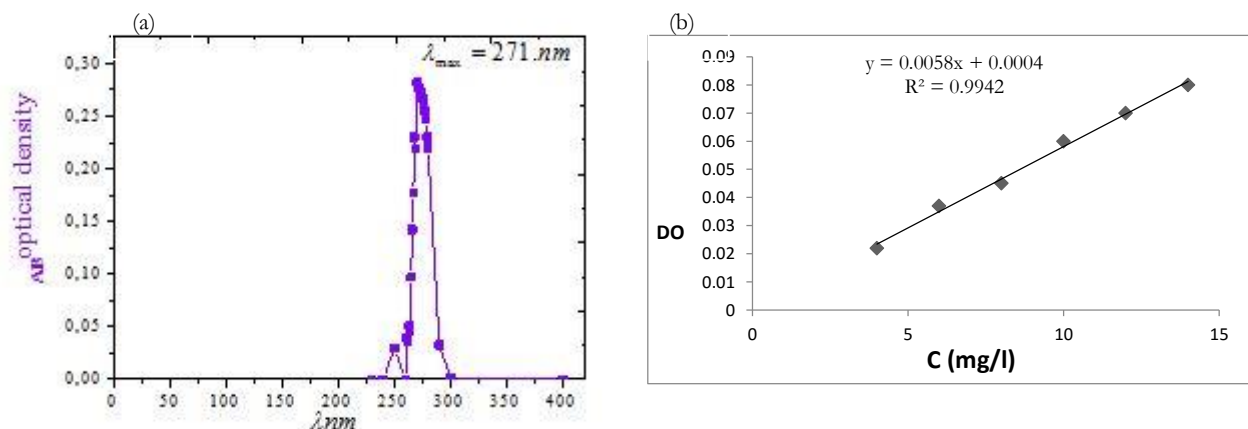| λ_{max}	269	270	271	272	273	274	275	276	277	278	279	280	300	400
DO	0,276	0.274	0.268	0.267	0.263	0.255	0.274	0.23	0.22	0.033	0.002	0.00	0.00	0.03

Figure 1. UV-visible spectrum of benzoic acid, Wavelength benzoic acid. (a) Wavelength benzoic acid,
((b) Curve benzoic acid calibration DO=0.0058 C_e + 0.0004

Modeling the adsorption isotherm (Kinetics and Thermodynamics) on the adsorption of benzoic acid of the activated coal and bentonite

Modeling of the equilibrium data was done using Freundlich and Langmuir isotherms. The Langmuir equation is the most widely used two-parameter equation, commonly expressed (Nakagawa, 2004)

$$\frac{c_{eq}}{q} = \frac{1}{k_l q_m} + \frac{C_{eq}}{q_m} \qquad (1) \qquad\qquad \frac{1}{x/m} = \frac{1}{q_m} + \frac{1}{q_m k_l} \cdot \frac{1}{C_{eq}} \qquad (2)$$

Where: Ceq = equilibrium concentration of adsorbate in solution after adsorption; x/m = amount adsorbed per adsorbent unit weight; and k_l and q_m are the Langmuir constants. From a plot of $Ceq/(x/m)$ versus Ceq, k_l (mg/g) and q_m (L/mg) can be determined from the slope and intercept, respectively. At equilibrium conditions, the adsorbed amount x/m can also be predicted using the Freundlich equation

$$\frac{x}{m} = k_F \cdot (C_{eq})^{1/n} \qquad (3) \qquad\qquad \log\frac{x}{m} = \log K_F + \frac{1}{n}\log C_{eq} \qquad (4)$$

Where k_f is an indication of the adsorbent capacity and $1/n$ is a measure of the surface heterogeneity, ranging between 0 and 1, becoming more heterogeneous as its value gets closer to zero. Using Eq. (3) from the plot of log x/m versus log C_{eq}, the parameters n and k were obtained from the slope and intercept, respectively. Since the analysis of the isotherm is important in order to develop an equation that accurately represents the results and which could be used for design purposes, two have been applied in this study, the Langmuir (1), Freundlich (2) out of the several isotherm equations. Adsorption model constants, the values which express the surface properties and affinity of the adsorbent, can be used for our Coal sample. The parameters in the models were estimated by nonlinear regression and by fitting transformed data to the linear forms of the models.

A total of 500 ml aqueous solution of benzoic acid definite initial concentration Ci equal to 70mg/l are contacted with a mass of 1g of crude coal, activated (NaOH, $ZnCl_2$, H_3PO_4) and Bentonite, under magnetic stirring at room temperature and pH = 4 for different contact times. When the equilibrium state of the solution thus prepared is reached, the solution undergoes a centrifugation 1500tr /min.

Influence of the mass of the (Coal and bentonite) on the adsorption of benzoic acid

The study is performed as above for the benzoic acid solution, for each mass (coal and bentonite) 0.2, 0.3, 0.4, 0.5, 0.8, 1g, the initial concentration of solution C_i = 70mg /l The mass of the activated coal (NaOH, $ZnCl_2$, and H_3PO_4) and optimum bentonite for benzoic acid is from (0.2-0.4) g the shape of the curves 03 having a vertical slope and linearity marked until the state of equilibrium. Isotherm of binding of benzoic acid on activated coal and bentonite 1g (coal activated by $ZnCl_2$, NaOH, H_3PO_4 and bentonite) each added material 100 ml of an aqueous solution of benzoic acid concentration definite the experiment is repeated with other benzoic acid concentration, 15, 20, 30, 40, 50, 60 and 70mg / l to only studies the influence of the concentration on the adsorption, the pH is kept constant at its optimum value (4), and the solution is stirred continuously. The Ceq concentration is measured by UV spectrophotometer.

Have been found that raw coal efficiency is not as important as the activated coal by (H_3PO_4, NaOH, $ZnCl_2$) and bentonite; because its efficiency of retention of benzoic acid at equilibrium is 2.81% after 70 min which is a value lower than that of activated coal (H_3PO_4, NaOH, $ZnCl_2$) and bentonite as retention yields of 40.98, 18.82, 17.3 and 49.3% respectively. Both coal treated with $ZnCl_2$ and NaOH have adsorption speeds 1,774 mg / l.mn and 2.014mg / l.mn successively; remarkable speed is raised to the sample of coal treated with ortho-phosphoric acid 3.98mg / l.mn. Benzoic acid has a better adsorption on coal treated with ortho-phosphoric acid, having a micro pore surface area greater than that of the modified bentonite, so increasing the porosity of the vase increases activated retention the benzoic acidThe maximum amounts absorbed by these three samples of the coal activated H_3PO_4, NaOH and $ZnCl_2$ are of the order of 14.34mg / g 6.16 mg / g and 6.58 mg / g respectively. This bentonite adsorption rate of 2.7 mg / l.mn and the maximum quantity fixed 6.9 mg / g. Thus, the clay, which has a high surface area, better adsorbed benzoic acid. Raw coal for the adsorption speed is 0.05mg / l.mn and the maximum quantity specified 0.98mg /g, we represent in the Figures 2c and Figure 2d. The adsorption isotherms of benzoic acid on the adsorbent of the raw coal, activated ($ZnCl_2$, NaOH, H_3PO_4) and Bentonite linearity's from the relationship Freundlich.

Absorption capacities of benzoic acid on these samples of the coal and the bentonite can be classified as follows: n Bentonite > n Coal (H_3PO_4)> n Coal ($ZnCL_2$)> n Coal (NaOH)> n raw Coal.

The residual coal treated with phosphoric acid gives the best results among the studied adsorbents studied. The figure 2d represent the Langmuir adsorption isotherm according to the relationship $\frac{1}{x/m} = \frac{1}{q_m} + \frac{1}{q_m k_l} \cdot \frac{1}{C_{eq}}$ there as the value 99% obtained for the factor that characterizes the linearity of the plot is estimated sufficiently acceptable to say that this isotherm obeys to model.

Table 7. Freundlich isotherm parameters for l'adsorption benzoic acid using coal (raw and enabled) and bentonite   n <1: low adsorbent n> 1: good adsorbent

Freundlich equation: $\log \frac{x}{m} = \log K_F + \frac{1}{n} \log C_{eq}$

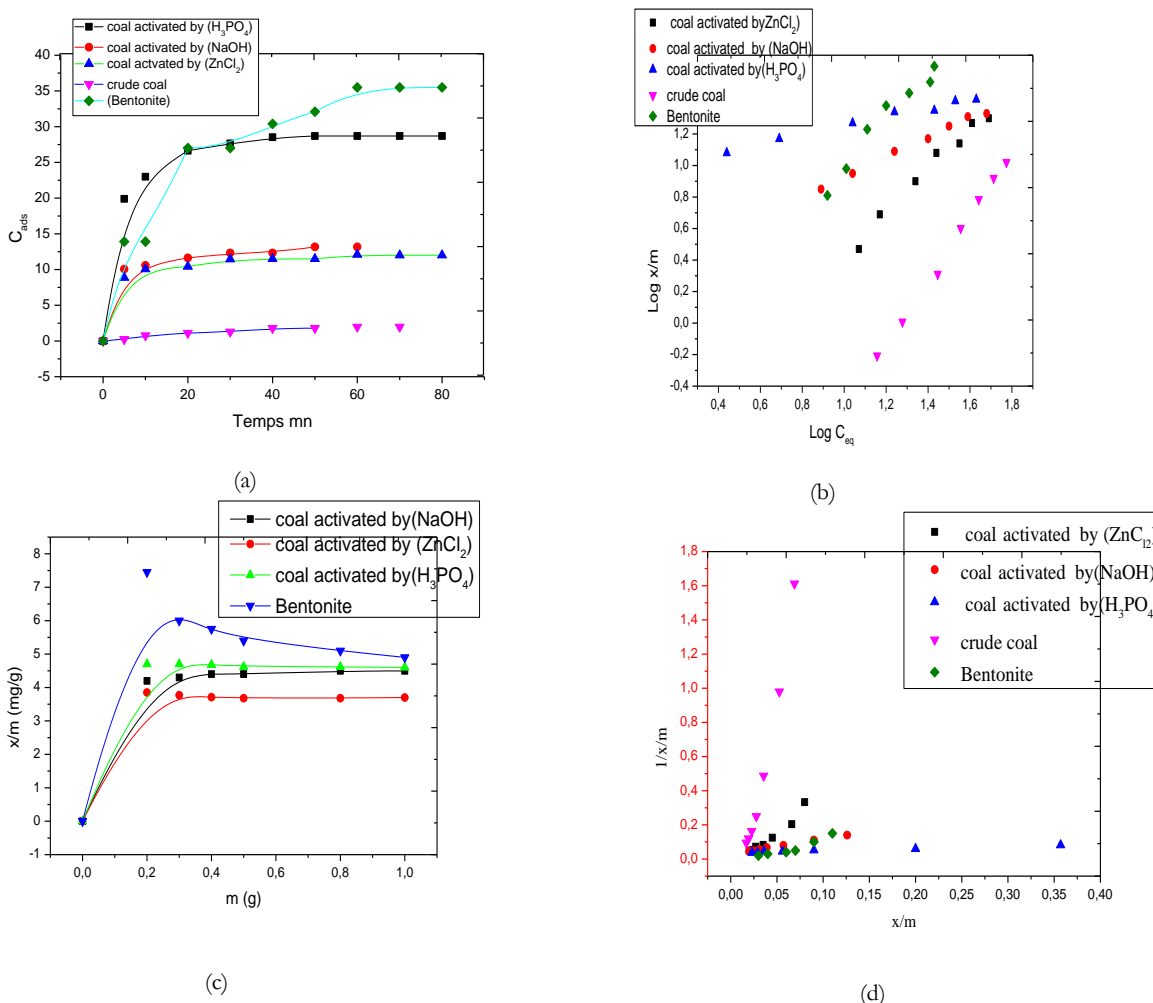|	n		Kf	R²
activated coal with $ZnCl_2$	0.75	low adsorbent	0.125	0.98
activated coal with H_3PO_4	3.53	good adsorbent	9.30	0.98
activated coal NaOH	1.99	good adsorbent	1.59	0.99
the raw coal	0.48	low adsorbent	0.002	0.98
Bentonite	3.5	good adsorbent	9.3	0.99

Figure 2. Freundlich and langmuir adsorption isotherm for benzoic acid by crude, activated Coals and Bentonite, (a) Effect of contact time on the removal of benzoic acid (Coal crude, activated and Bentonite), (b) Freundlich adsorption isotherm for benzoic acid by crude, activated Coals and Bentonite, (c) Influence of the mass (the activated coal and the modified bentonite) on the removal of benzoic acid, (d) Langmuir adsorption isotherm for benzoic acid by activated, raw coal and Bentonite

Conclusions

This work show the interest of the local clay and coal (from Algeria) in environmental technology for the treatment of Composed Organic (benzoic acid) which originates from an industrial pollution (petrochemical plants, refineries, paper mills).The abundance of clay material is not the only advantage, but it's really a cost-effective natural adsorbent for organic compounds. The abundance of clay material is not the only advantage, but it's really a cost-effective natural adsorbent for organic compounds. The adsorption of benzoic acid was studied by following the method of spectrophotometric assay method. Adsorption tests of benzoic acid indicate that bentonite and coal can be used as adsorbent of organic compounds given its abundance and low cost. For the same concentration and for the same flow rate, the time to breakthrough and saturation increases with increasing retention. Models of Langmuir, and FREUNDLICH were applied to the experimental data obtained from thermodynamic studies of fixed bed to provide the breakthrough curves. All models are generally well simulated to describe all or part breakthroughs curves of benzoic acid on clay and natural coal Algeria.

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