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Phenol adsorption on Ca / activated carbon catalysts: effect of formic acid

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Abstract

The monometallic performances of catalysts containing calcium Ca (II) supported on the activated carbon (CA) prepared by the method of impregnation to eliminate involved phenol or not from formic acid starting from a phenol water charged were studied by the technique of adsorption. The support (CA) and the Ca/CA catalyst were characterized by BET, IRTF and AAS. The effects of the pH of catalysts and the content of metal calcium were studied. The experiments of adsorption made it possible to indicate the best catalysts 3%Ca/CA (99.41%) to pH = 1 in absence of formic acid and 3%Ca/CA (96.75%) pH=7 in the presence of formic acid. From where, the capacities of adsorption of phenol of catalysts showed that the formic acid significantly did not improve the properties of surface of the X%Ca/CA catalysts.

Key words: Adsorption of phenol, calcium, activated carbon and formic acid.

INTRODUCTION

Agricultural waste not easily biodegradable and abundantly available in Ivory Coast is rejected into our environment. Bamba (Bamba and al., 2008), Athéba (Athéba and al., 2012) showed that the activated carbon (CA) could be obtained starting from the residues of coconuts. The problem of the contamination of water by the phenolic compounds worries more and more. Faced with this growing concern, it is therefore necessary to develop new high-performance materials capable of meeting the requirements related to sustainable development and the preservation of the ecosystem. The heterogeneous catalysts containing the biomass could be a true advantage for the decontamination of water by the phenolic compounds. Several methods such as adsorption (Robberson and al., 2006) (Lászlo, 2005), chemical oxidation (Karpel and al., 2000), flocculation of coagulation (Byun and al., 2005) were already used to eliminate the phenolic derivatives from waste waters. Among all these methods, adsorption seems to be simpler and less expensive. The process more used for the treatment of waste waters relates to the methods of adsorption. Indeed, during last years, a large variety of materials such as the activated carbon (Nakagawa and al., 2004) (Warta and al., 1995) (Su and al., 2005) (Pan and al., 2005), silica (Zhao and al. 1994) (Parida and al., 2006), polymeric resins (Zhang and al., 2006) (Delval and al., 2006), fly-ashes (Wang and al., 2005), clays whose kaolinite (Alkaram and al., 2005), and zeolites (Koubaissy and al., 2011) (Khalid and al., 2004) (Koubaissy and al., 2008) (Koubaissy and al., 2011) (Koubaissy and al., 2012), were explored in detail for the elimination of the phenolic pollutants of waste waters.

The originality of this work is the use of heterogeneous catalysts monometallic like adsorbent materials to cleanse a water charged with phenol molecules.

2 EXPERIMENTAL

2.1 Preparation of activated carbon

The coconut husks, used as raw material are initially carbonized with 550°C in the oven during one hour. The carbonized materials have a percentage of carbon of 80%.

Carbonized is crushed in a porcelain mortar. After carbonization then crushing of the hulls, coal is placed in an electric sifter for the sorting of the grains according to their diameters. During these manipulations, we used coal with particle sizes less than or equal to 125 µm. Physical activation was used in this work. A quantity of coal was weighed and calcined at 650°C in an oven in the presence of vapor during 1 hour (Figure 1). Once finished activation, one carries out the washing of the sample until pH = 7. The sample is then dried with the drying oven during 1 h at 120°C.

Figure 1: Activated carbon left the oven

2.2. Ca-supported catalyst on activated carbon support

The metal used to prepare our monometallic catalyst is calcium. Stock solutions of given calcium concentration are prepared from hydrated calcium chloride ($CaCl_2$, $2H_2O$). The method used is the ion exchange impregnation technique from the precursor ($CaCl_2$, $2H_2O$). A quantity of metal salt is then introduced into an aqueous suspension of activated carbon. The pH is adjusted by adding a solution of HCl or KOH in order to activate the adsorption sites of the support. The whole is stirred for 24 hours. After exchange, the impregnated support is filtered on Buchner and dried in an oven at 105°C for 6 hours. Suspending makes it possible to avoid agglomeration of the oxide grains, to promote contact between the support and the precursor and to optimize the dispersion of the active phase. The monometallic catalyst 3%Ca/CA is activated at 400°C. with a temperature rise rate of 1°C/min for 4 hours.

2.3 Determination of the concentration of phenol by colorimetric proportioning

The concentrations of phenol are measured by the colorimetric method of the 4-aminoantipyrine developed by Emerson in 1943 (Emerson, 1943).
This method is of everyday usage for the colorimetric determination of phenols in various materials because of its sensitivity, its speed, the absence of hard stages and its cost relatively low (Svobodova and Gasparie, 1971). The phenolic compounds, react with the 4-AAP in the presence of potassium hexacyanoferrate ($K_3Fe(CN)_6$) like oxidant under alkaline conditions and give a complex coloured pink having a maximum of absorptance to 510 nm.

Two beakers containing 50 ml of aqueous phenol solution were used, 1 g of catalyst 4%Ca/TiO_2 was introduced into each beaker. Formic acid was added to the one of the beakers. After 3 hours under agitation, the mixtures are filtered on funnel and the phenol concentrations in solution are determined by spectrophotometry UV/VIS with 510 nm.

2.4. Characterization of the support and catalysts

The results of analyses of moistures, the rates of ash and the densities of rough materials and the studied activated carbon are indicated in table 1.

Table 1: Moisture content, ash content and density of the raw and active coal studied.

Samples	Gross	Active
Water content	5.3	1.7
Rate of ash	0.16	2.9
Density	0.807	0.695

2.4.1 Determination of zero point charge pH(zpc)

The zero point charge pH(zpc) corresponds to the pH value for which the net charge of the surface of the adsorbents is zero. This parameter is very important in adsorption phenomena, especially when electrostatic forces are involved in the mechanisms. Indeed, the zero point charge pH (zpc) is the pH at which the surface charge due to the H_3O^+ and OH^- ions vanishes. The nature of activated charcoal can be acidic, neutral or basic depending on pH (zpc).

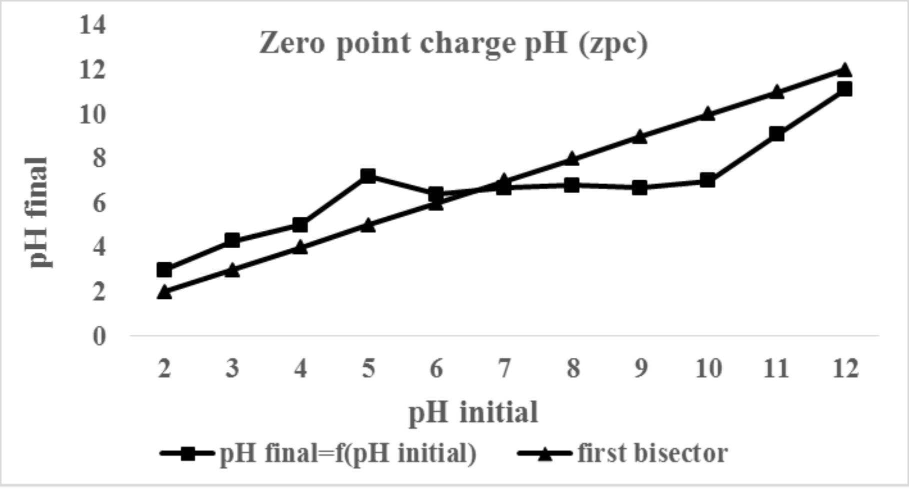

Figure 2: Zero point charge (Pzpc)

The zero point charge pH(zpc) of activated carbon in our study was estimated at pH ~ 6.6 (Figure 2). The results are similar to those reported in the literature on shea butter cakes, where pH (zpc) are close to 6.7 (Tchakala and al., 2012).

3. RESULTS AND DISCUSSION

3.1. Textural analysis

The isotherms adsorption and desorption of N_2 of the support (CA) and catalyst with various calcium contents (X%) are represented on figures 3 and 4. The isotherm of adsorption of the activated carbon (CA) represented on figure 3 is characteristic with a microporous adsorbent material of which the pores fill with very low pressures. This one is typical of the highly microporous adsorbents of type I according to the classification of IUPAC. In agreement with the nomenclature defined by the IUPAC, the isotherm of N_2 adsorption and desorption of the X%Ca/CA catalyst also of type I. This type of isotherm is typically characteristic of microporous materials; this indicates that the microporous structure of CA is retained or preserved after addition of calcium. Moreover, figure 3 shows that the distribution of the size of the pores of catalyst for the calcium content of X% is similar to that of the pure activated carbon. The specific surface of catalyst containing calcium (X%Ca/CA) is higher than that of the activated carbon (CA), (Table 2); this increase in specific surface would be probably due to an increase in micropores after calcium addition on the activated carbon.

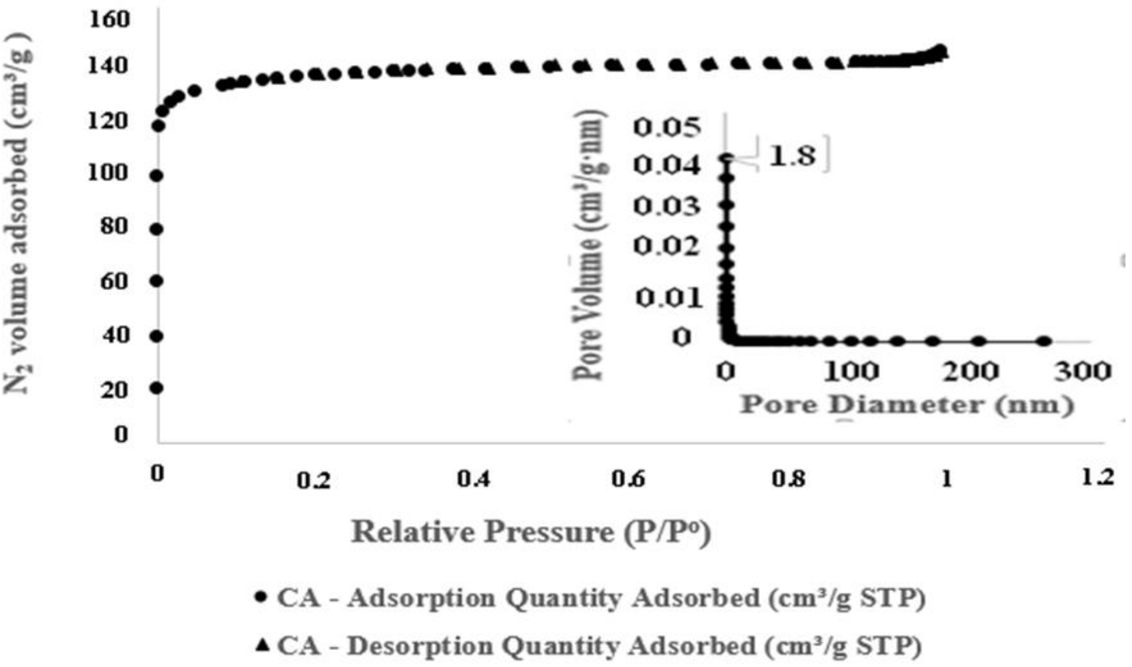

Figure 3: Isotherm of adsorption-desorption and distribution of size of activated carbon (CA)

The shape of the distribution curve of the pore size of the activated carbon confirms the microporous nature of the solid, with a porosity of 1.7 nm. This corroborates with that of Attéba and al. (Athéba and al., 2012).

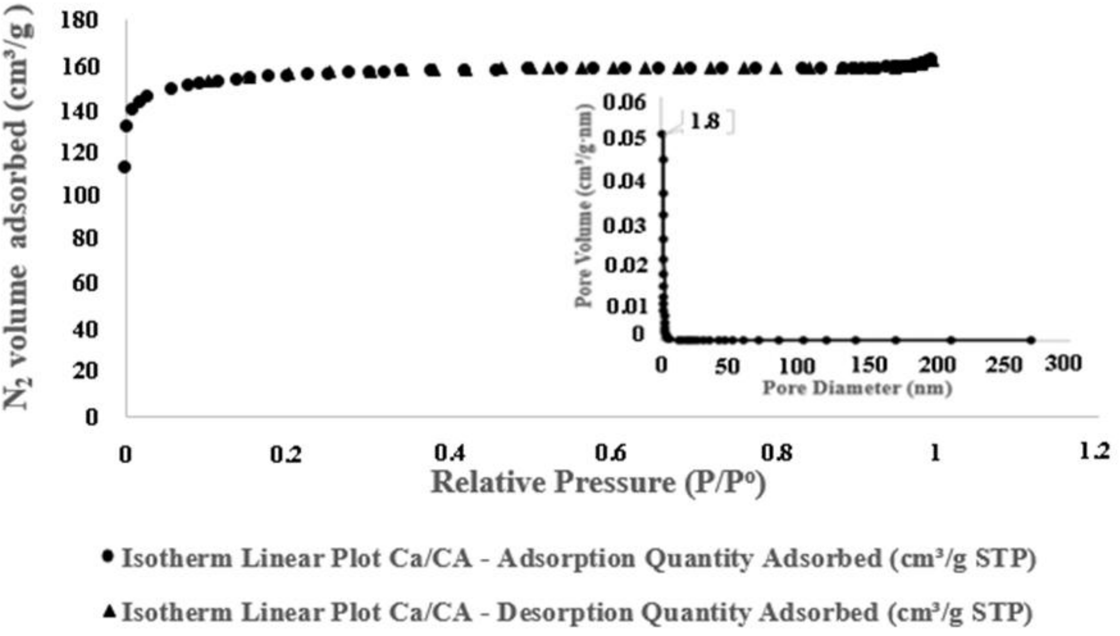

Figure 4: Isotherm of adsorption-desorion and distribution of size of %Ca/CA

Table 2: Textural Properties of CA Support and Catalyst 3% Ca/CA

Solids	**S_{BET} (m^2/g)**	**D_p (nm)**	**V_p (Cm^3/g)**
Actived carbon (CA)	441	1.8	0.22
Catalyst 3%Ca/CA	504	1.8	0.25

3.2 Infrared spectroscopic characterization (FTIR) of CA and 3% Ca/CA

In order to study the chemical functions present in the prepared adsorbent, we used Fourier transform infrared spectroscopy. The infrared spectrum of activated carbon before adsorption shows the presence of characteristic bands between 400 and 4000 cm^{-1}.

The infrared spectrum of the activated carbon obtained by physical activation is given by figures 5 and 6. These spectra are characterized by the following spectral bands:

Figure 6 shows a slight shift by the presence of a small intensity band at 3674.79 cm^{-1} against 3615.55 cm^{-1} of the AC support that could be attributed the binding of OH ($\nu_{O\text{-}H}$) functions carboxylic acid, alcohol, phenol and water after the introduction of calcium.

We observe several bands 2987.36, 2971.88 and 2893.37 cm^{-1} against 2189.36 cm^{-1} of the CA support resulting mainly from the aliphatic C-H elongation vibrations, in the aromatic groups. On the spectrum of the CA (Figure 5), it appears at 1696.65 cm^{-1} a band that could be attributed to the vibrations of the bonds C = O (carboxylic acid, anhydride, lactone, ketone) but which does not appear on the spectrum 3% Ca/CA (Figure 6) this can be explained by the presence of calcium metal. It should be noted that the presence of a very low absorption peak observed at 1451.43 cm^{-1} compared to 1581.92 cm^{-1} corresponds to the elongation of the C=C bond of aromatic rings, this peak is slightly displaced due to the presence of the calcium atom in relation to that of activated carbon. The absorption zone (region) at 1406.36, 1393.84 and 1382.24 cm^{-1} versus 1424.54 cm^{-1} of the support could be attributed to the characteristic elongation of the OH ($\delta_{O\text{-}H}$) linkage carboxylic acids. The 1250.76, 1242.63 and 1229.69 cm^{-1} region compared with 1176.87 cm^{-1} of the CA support could be attributed to the elongation of the C-O bond ($\nu_{C\text{-}O}$) characteristic of carboxylic acids. The zone of adsorption located at 1075.45, 1066.15 and 1055.46 cm^{-1} would be characteristic of the deformation in the plan of CO aliphatic (ethers, phenols). A light shift between 892.57 to 406.52 cm^{-1} due to the presence of calcium against 874.67 to 424.75 cm^{-1} of the support CA, would be due to the absorption of the vibrations of deformation out of plan of the aromatic CH connections (γ_{CH}). According to the light shifts of the bands of adsorption compared to those of figures 5 and 6, the FTIR spectrum would prove that the calcium is incorporated in the pores of the CA.

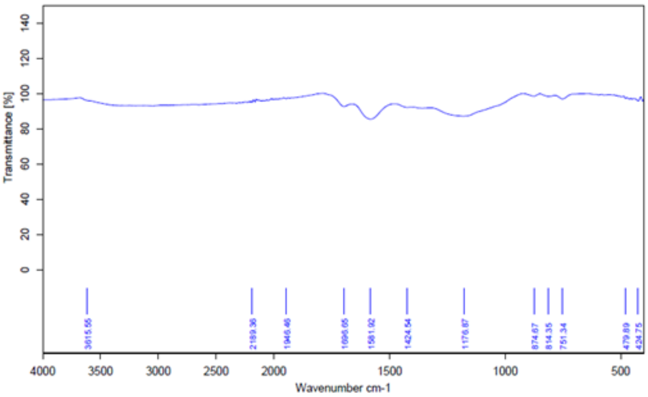

Figure 5: FTIR spectrum of CA

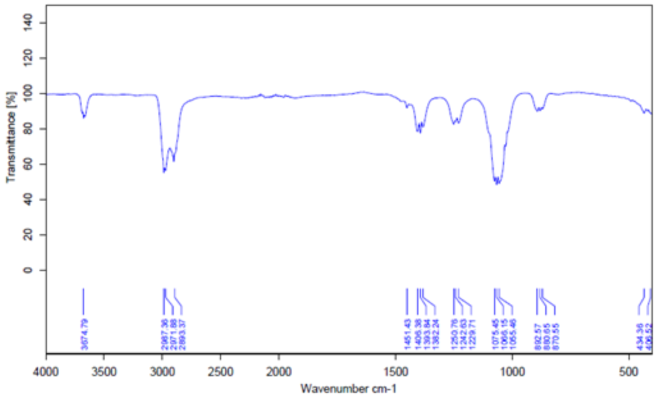

Figure 6: FTIR spectrum of 3%Ca/CA

3.3 supported Catalysts monometallic: Ca/CA

The deposit of each metal on the activated carbon with different pH (1, 5, 7, 9 and 12) is carried out with the introduced initial contents of 1%Ca with 5%Ca.

3.3.1 Effect of the pH and the content (%)

In this research task we were interested in the effect of the pH and the content of metal calcium (Ca) deposited on the activated carbon by the method of impregnation. The adsorption of metals on the dioxide of calcined commercial titanium with different pH (1, 5, 7, 9 and 12) is carried out with the various introduced initial contents. The got results are represented on the figure 5 below.

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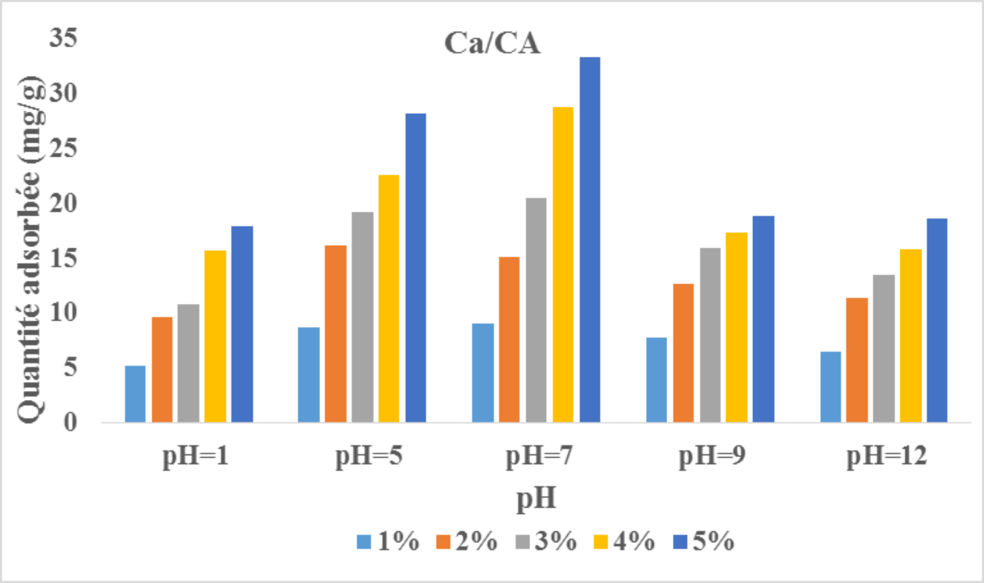


Figure 8: Effect of pH and content (%) on calcium adsorption on activated carbon

The results obtained in figure 8 reveal that the adsorption rate of calcium increases considerably when the pH tends to 7 and then decreases to pH 9 and 12. This can be explained by the fact that at a strongly acid pH (pH = 1), the adsorption is negligible. Indeed, the concentration of H^+ protons is high in solution which induces their competition with Ca^{2+} cations for the free sites that exist at the surface of the adsorbent supposedly positively charged. So there is an electrostatic repulsion between the cations and the positively charged surface. At pH = 5: the concentration of the H^+ protons decreases whereas that of the Ca^{2+} cations remains constant, which explains the increase in the adsorption rate. At pH = 7, calcium adsorption reaches a maximum. This observation is consistent with that of the study by Anirudhan et al (Anirudhan and Sreekumari, 2011) who showed in their study that at pH ≤ 5, the adsorption of metals is not favored but that the optimal pH values for a given maximum adsorption was 6-7, respectively. Indeed, Budinova (Budinova and al., 1994) consider that the isoelectric point of the support is located in the pH zone corresponding to the rapid increase of the adsorption capacity. For the support used in these experiments the isoelectric point is between pH = 6 and 7. Some authors have found that the pH value at the isoelectric point of different carbons is between 4.75-7.10 as quoted by Budinova (Budinova and al., 1994). At pH = 9 and 12, the adsorption rate decreases considerably because we begin to approach the precipitation pH of the calcium and copper ions Ca^{2+} with OH^- ions to form $Ca(OH)_2$ complexes. Finally, we also observe that the amount of metal adsorbed by activated carbon varies according to the content introduced into solution.

3.4 Adsorption of phenol by X% Ca / CA catalysts

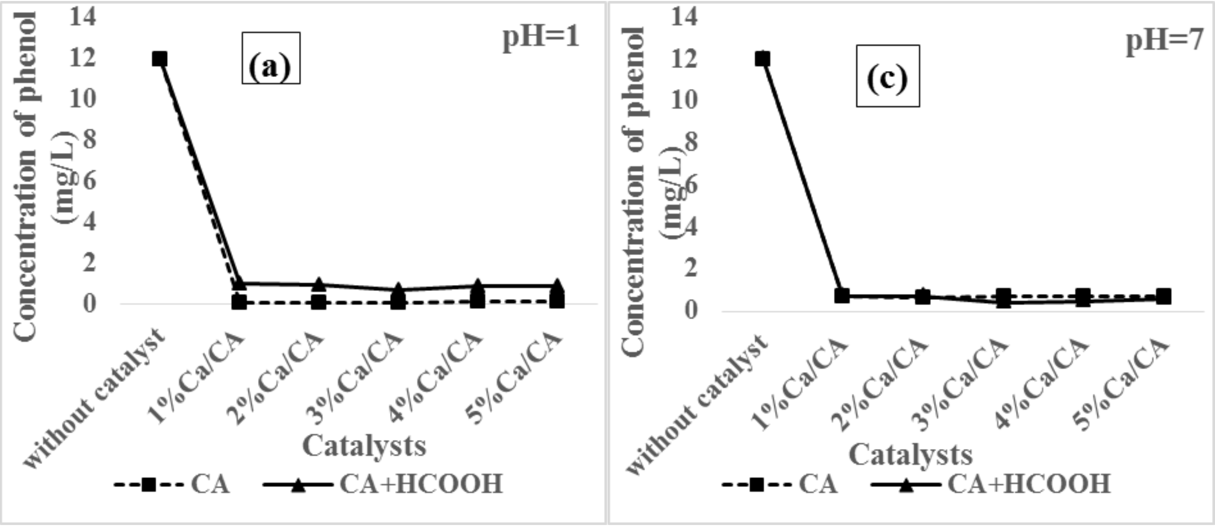
From these results, it is noted that monometallic Ca/CA catalysts are even more efficient in the absence of formic acid (HCOOH).

- **Absence of formic acid (HCOOH)**

Indeed, at pH =1, the adsorption rate of phenol by Ca/CA catalysts is higher because the adsorption mechanism of the phenol molecules on the catalyst surface would be due via the hydrogen bonds between the catalysts functions (groups) -OH of phenol and hydrogen ions H^+ of the catalyst surface 3%Ca/CA at pH = 1. Also, the presence of H^+ and Ca^{2+} ions on the surface of the catalysts would benefit H^+ ions more to form the hydrogen bonds with the hydroxyl -OH function (group) of the phenol. It should be noted that the activity of the Ca/CA catalysts in basic medium (pH = 9 and 12) decreases. This is due to the electrostatic repulsion between the OH^- ions on the surface of the catalysts and the phenolate ions $C_6H_5O^-$.

- **Presence of formic acid (HCOOH)**

The presence of formic acid (HCOOH) promotes an increase in the rate of adsorption of phenol for catalysts at pH = 7 because the ions OH^- being reduced the ions Ca^{2+} and the ions $C_6H_5O^-$ attract and there is also possibility of formation of hydrogen bonds. Ca/CA catalysts in a very acidic medium (pH =1 and 5) favor less the adsorption of phenol this is explained by the fact that the H^+ and Ca^{2+} ions could be in competition therefore favoring an environment hostile to adsorption. Thus, for the catalysts at pH = 9 and 12, the adsorption rate decreases considerably that would be due to the electrostatic repulsion between the ions OH^- at the surface of the catalysts could be related to the clogging of the pores of the latter by the presence of formic acid.



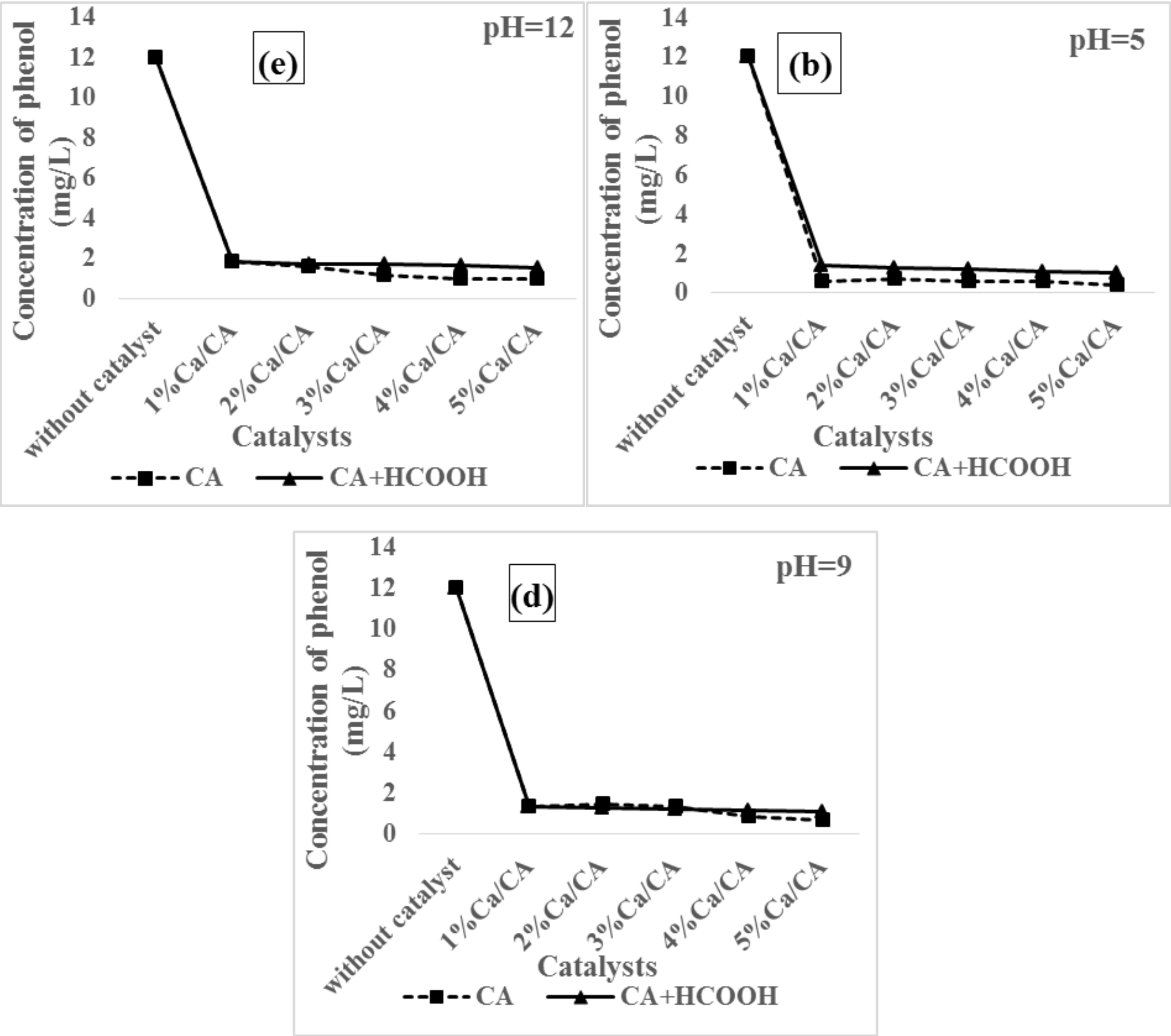


Figure 9: Adsorption of phenol by Ca/CA catalysts without formic acid (■) and in the presence of formic acid (▲) at different pH: (a) pH = 1, (b) pH = 5, (c) pH = 7, (d) pH = 9, (e) pH = 12.

CONCLUSIONS

The study of adsorption of phenol by catalysts supported containing calcium (Ca) on the activated carbon (CA) showed a better catalytic performance in presence or absence of formic acid. On the other hand, in absence of formic acid the catalysts monometallic Ca/CA are more favorable to the adsorption of phenol. Finally, the best catalysts selected are 3%Ca/CA with pH = 1 and 3%Ca/CA with pH = 7 respectively in absence and in the presence of formic acid.

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