

Heterogenization of Copper Catalyst for the Oxidation of Phenol, a Common Contaminant in Industrial Wastewater

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Advance oxidation process was employed as a pretreatment of industrial wastewater. For this purpose, the use of heavy metals as a catalyst is necessary but also complicated because homogeneous catalysts are difficult to recover after reaction process. The heterogenization of Cu(II) ions was proposed by taking advantage of the adsorptive characteristics of polymeric matrices. Crosslinked poly(4-vinylpyridine) of 2 and 25% and poly(D-glucosamine) were tested as supports of copper. Adsorption was employed to heterogenize Cu(II) by considering the influences of pH and temperature on the process. The catalysts were evaluated by their metal content, catalytic behavior for the oxidation of phenol and leaching degree after reaction. Poly(4-vinylpyridine) 2% was the best material for Cu(II) immobilization with an adsorption capacity of 90 mg g⁻¹. Afterward, poly(4-vinylpyridine) 2%, Cu(II) achieved 64% of phenol conversion, which represents a favorable result for the oxidation of phenol as the model of industrial wastewater pretreatments. © 2012 American Institute of Chemical Engineers Environ Prog, 32: 269–278, 2013

Keywords: poly(4-vinylpyridine), chitosan, copper catalyst, adsorption, phenol removal

INTRODUCTION

The application of conventional homogeneous catalysts becomes complicated in practice due to some problems, which were represented by the catalytic separation after use, catalytic regeneration, etc [1]. To overcome these problems, it was proposed to use heterogeneous catalysts on oxidation processes, also called heterogeneous catalytic systems [1]. Interesting results reported to use transition metals as active phase over zeolites [2], pillared clays [3, 4], or activated carbon as supports [5]. The main problem of these catalysts comes from the leaching of the metals when oxidation was carried out at low pH, below 3. Nowadays, catalyst-based technologies present an optimized activity due to they intend to achieve clean processes without by-products, eliminating the need of waste disposal [6]. For instance, various supports anchor metal complexes, from which polymer supports provide better catalytic activity and selectivity [7]. The catalytic activity of copper ion in

peroxide activation was dramatically enhanced by complexation with pyridine, organic acids, amino acids, and other chelating acids [8]. Therefore, Cu(II) was selected as catalyst for the catalytic oxidation of recalcitrant compounds.

The heterogenization of homogeneous catalysts develops and easy handling in different catalytic reactions [9, 10]. The study of metal complexation is increasing [11, 12], although among the variety of heterogenization techniques, the adsorption better supports ion species onto polymeric matrices. The efficiency of the oxidation reaction depends on the catalytic activity mostly disturbed by the leaching of the metal content [13]. Therefore, the selection of the adsorbent directs the effectiveness of the Cu(II) heterogenization.

The polymers attract special interest as supports because they have a rigid and crosslinked network where catalytic metals were attached [14], and where catalytic properties were preserved. The sorption onto materials of biological origin was recognized as an emerging technique [12, 15, 16]. Materials such as poly(4-vinylpyridine) (PVP) and poly(D-glucosamine) were selected as catalytic supports because of their pyridyl and amino radicals.

PVP with a structural formula presented in Figure 1a, is a very efficient adsorbent due to its pyridyl group has a strong affinity with metals. The three-dimensional and the long chain structure of PVP provides a molecule trap, which is beneficial to maintain the interaction between Cu(II) and polymeric surface [17]. For this reason, PVP was studied as a ligand of metals to form soluble homogeneous complexes [18, 19], although its adsorption capacity and catalytic activity as a heterogeneous catalyst is still unknown.

Normally, adsorption studies employ synthetic polymers but an important effort is being devoted to use biopolymers instead [20]. The biopolymer group includes materials such as starch derivatives, gelatin, cellulose, derivatives of chitin, and chitosan materials [21]. Chitosan (Figure 1b) is a partially acetylated glucosamine biopolymer resulting from the alkaline deacetylation of Chitin (poly(*N*-acetyl- β -D-glucosamine)), which is the second most abundant biopolymer in nature close to cellulose [20]. Chitosan actually is a heteropolymer containing both glucosamine and acetylglucosamine units. The presence of amine groups explains its affinity for metal ions. Based on a previous report [21], chitosan is a promising support due to its affinity with metals and its lack of diffusion problems when it was used as a catalyst.

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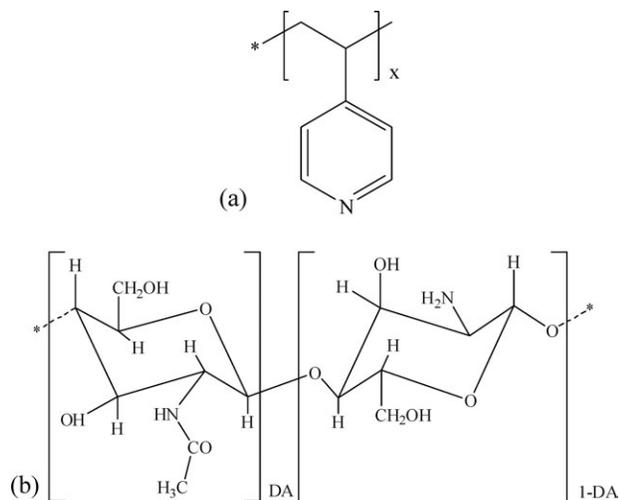


Figure 1. Structural formulas of (a) poly(4-vinylpyridine) structural formula and (b) poly(D-glucosamine).

The aim of this work is to perform and evaluate the heterogenization of homogeneous catalysts by the adsorption of Cu(II) over polymeric materials. For this purpose, the influence of variables such as the polymeric support, pH, and temperature was evaluated in order to obtain a suitable catalyst capable to promote the wet oxidation of recalcitrant compounds without metal release.

MATERIALS AND METHODS

Materials

PVP 2% crosslinked powder (PVP₂; Ref. 81391) and PVP 25% crosslinked beads (PVP₂₅; Ref. 81393) were purchased from Sigma-Aldrich. As indicated in the technical sheet from Sigma-Aldrich, both PVP 2% and 25% are crosslinked with divinylbenzene. Chitosan beads were supplied by E. Guibal (Laboratoire de Génie de l'Environnement Industriel, Ecole des Mines d'Alès, France) and synthesized according to an original procedure [22]. Copper sulfate pent hydrated with 99% of purity (CuSO₄·5H₂O) was obtained from Sigma-Aldrich, while hydrochloric acid (HCl) 2N standard solution and sulfuric acid (H₂SO₄) 99% were purchased from Fluka. Phenol 99% and hydrogen peroxide (H₂O₂) 30% (w/v; 100 vol.) PA were purchased from Panreac. Distilled water was used for all reagent solutions and employed as solvent.

Methods

The heterogenization of Cu(II) was performed by using a batch adsorption system, which consists of six beakers of 250 mL submerged in a thermostatic water bath, Figure 2. A mother solution with a high concentration of 1.0 g L⁻¹ of Cu(II) was prepared by dissolving copper sulfate in distilled water. Six solutions with different Cu(II) concentrations (0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 g L⁻¹) of 0.2 L were prepared by diluting the mother solution in distilled water to the correct concentration. Every batch adsorption system was agitated with a magnetic stirrer (90 rpm) for 5 h at 20, 30, and 40°C. As the purpose of the research is to work at soft conditions, avoiding energy expenses, the use of the catalyst was made at mild conditions as well. It would be possible to use higher temperatures, as far as the polymer matrices will not be destroyed. The pH was measured twice, before the polymer was put in contact with the Cu(II) solutions and at the end of the adsorption period. The adsorption begin when 1 g of

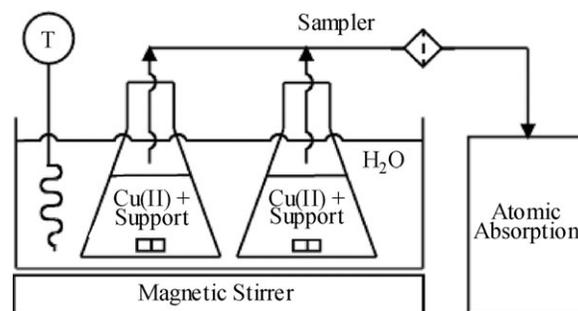


Figure 2. Batch adsorption set-up for the heterogenization of homogeneous catalysts.

the adsorbent was added into each of the six Cu(II) solutions. Samples of 0.1 mL were taken with a syringe and filtered (45 μm pore membrane) at different time intervals to control the residual Cu(II) concentration in the supernatant. Cu(II) concentration was determined by analyzing the samples in an Atomic absorption spectrometer. After 5 h, the polymer-Cu(II) material was recovered by filtration (150 nm pore membrane), then cleaned with distilled water, dried at room temperature for 24 h and stored in a dry container.

Catalytic Oxidation

The catalytic oxidation of phenol was conducted at 30°C in a batch stirred tank reactor of 500 mL in volume at atmospheric pressure. The initial phenol concentration was 1 g L⁻¹ and H₂O₂ was used as the oxidant at the stoichiometric phenol/peroxide (Ph:H₂O₂) molar ratio (1:14). The mass of the added catalyst was equivalent to 50 mg L⁻¹ of Cu(II) in solution.

After the selection of the best catalyst, the process was performed at pH 6 by using a buffer solution of NaOH and K₂HPO₄. Reaction progress was monitored by withdrawing 5 mL samples for 2 h of reaction, and then analyzed by HPLC and Atomic absorption to determine the remaining concentration of phenol and copper, respectively.

Analytical Procedure

The residual Cu(II) concentration in the supernatant was determined by an Atomic Absorption Spectrometer (Perkin Elmer, model 3110) (AA) with a specific lamp for the element of copper (Perkin Elmer, Ref. 01074). The samples were diluted in order to avoid saturation of the detector signal for the case of copper concentrations more than 10 mg·L⁻¹. The dilution of samples was made with a solution of HCl 1%. The analyses were performed at 325 nm of wavelength [23]. The calibration curve was performed using various standards of known Cu(II) concentration.

Infrared spectroscopy was made using a Perkin-Elmer-Spectrum spectrometer. The preparation of the samples was based on grinding the polymers until powder. Then, the powder was directly analyzed using a diamond cell.

RESULTS AND DISCUSSION

The adsorption capacity of Cu(II) is the basic variable to be considered on the evaluation of the heterogenization of Cu(II). The adsorption capacities (*q*) of Cu(II) onto PVP₂, PVP₂₅, and chitosan were calculated by a mass balance where the initial (*C*₀) and final (*C*_e) concentration (g L⁻¹) of Cu(II), the volume (*V*) of bulk solution (mL), and the mass (*m*) of the adsorbent (*g*) were correlated by Eq. 1:

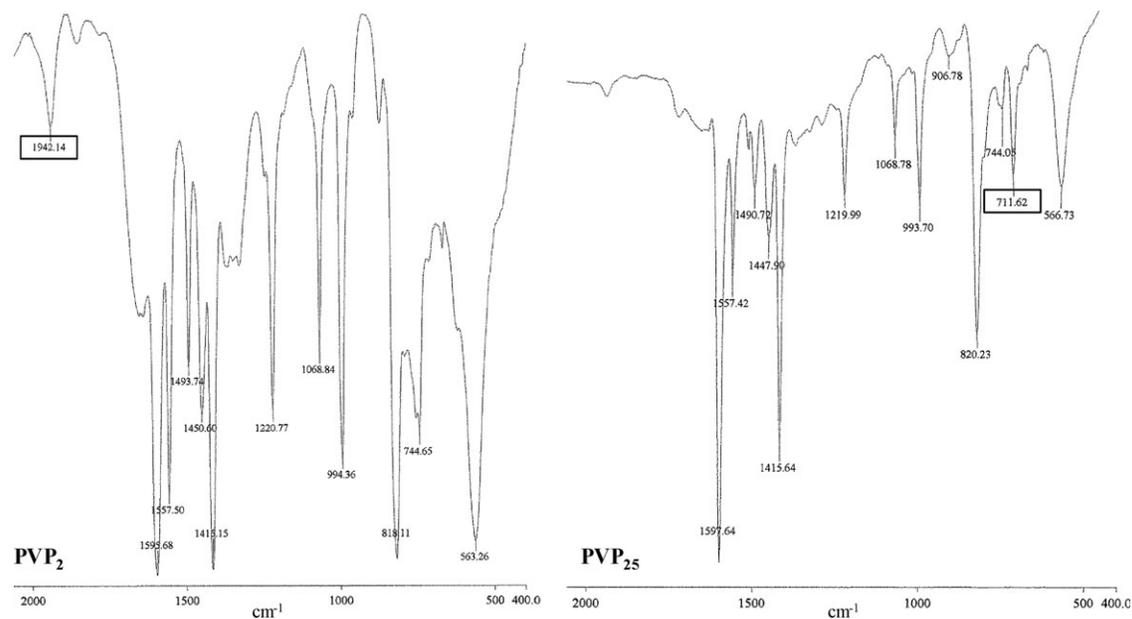


Figure 3. FTIR spectra between 2000 and 400 cm^{-1} of PVP₂ and PVP₂₅.

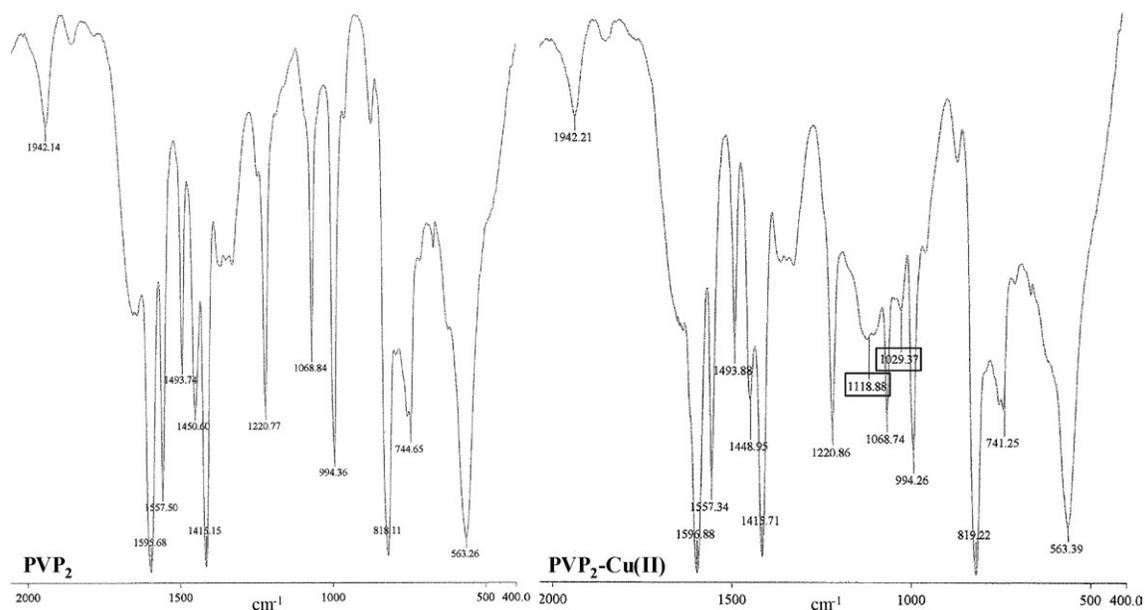


Figure 4. FTIR spectra between 2000 and 400 cm^{-1} of PVP₂ and PVP₂-Cu(II).

$$q = \frac{C_0 - C_e}{m} \cdot V \quad (1)$$

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The characterization of PVP-support by FTIR was made to detect the differences existing between PVP₂ and PVP₂₅. The Figure 3 presents the FTIR absorption spectrum of PVP₂ and PVP₂₅ against an arbitrary transmittance. From the differences of vibrations signals, PVP₂ presented a vibration at 1942 cm^{-1} , which reflects the presence of substituted double bonds on its matrix, confirming the substitution pattern of a benzene nucleus. For the case of PVP₂₅, it appears a vibration at 711 cm^{-1} absorption band,

which can be assigned to out-of-plane bending and describes the orientation of the aromatic rings with five adjacent hydrogen atoms, promoted by its 25% of cross-linking. These characteristics have been observed for metal loading purposes [24, 25].

In Figure 4, it is presented the FTIR spectra of PVP₂ and the catalyst (PVP₂-Cu(II)). It can be observed two characteristic vibration signals at 1029 and 1118 cm^{-1} . Vibration at 1029 cm^{-1} band was assigned to the Cu(II) presence on the matrix that causes some changes on the pyridine ring orientation [25]. Absorption band at 1118 cm^{-1} was assigned to the stretching and bending of S—O vibration of SO_4^{2-} [25]. FTIR spectra of PVP₂₅ and PVP₂₅-Cu(II) were also evaluated and the presence of Cu(II) and SO_4^{2-} is evident at the same vibration bands as for PVP₂-Cu(II).

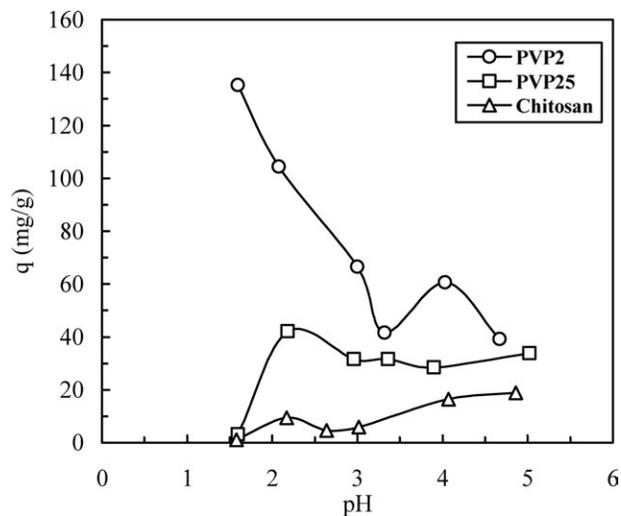


Figure 5. Adsorption capacity of Cu(II) onto PVP₂, PVP₂₅, and chitosan. [Cu(II)]₀ = 0.1–1.0 g L⁻¹ for PVPs and [Cu(II)]₀ = 0.01–0.10 g L⁻¹ for chitosan, *m* = 1 g, *T* = 30°C, as a function of pH.

From the above, differences between PVP₂ and PVP₂₅ do not seem important for the adsorption of Cu(II); therefore, it is essential to evaluate the influence of variables such as temperature, pH, or initial Cu(II) concentrations.

Effect of the pH on the Heterogenization

During the adsorption of Cu(II), the pH values of the solution at equilibrium changed from pH 5.0 to 5.5, values that describe a stable pH system. The small pH change describes the competition of Cu(II) and H₃O⁺ for binding to available sites in the polymer surface [15]. The behavior of each support at different pH is important because the catalyst (Cu(II)-support) was planned to interact in a variable pH media, such as the oxidation. Figure 5 shows the adsorption capacities of PVP₂, PVP₂₅, and chitosan as a function of the pH. Sulfuric acid was used to adjust the pH of Cu(II) solutions. The removal of Cu(II) at 20°C was evaluated at pH < 5 because of the distribution of Cu(II) species (Figure 6). Copper precipitation appears as hydroxide at values above pH 5 with the initial Cu(II) concentration of 1 g L⁻¹ (15.7 mM). Results show that Cu(II) adsorption presents different behavior depending on each adsorbent. For the case of PVP₂, the adsorption capacity declines when pH was increased, presenting better results on acid media, up to 140 mg g⁻¹. PVP₂₅ presents values around 40 mg g⁻¹ between pH 2 to 5, but at pH < 2 the adsorption capacity was negligible because the acid media with high content of H₃O⁺ ions compete with Cu(II) for the formation of bonds with available radicals of PVP₂₅. However, chitosan presented better results at pH 5 (20 mg g⁻¹) where Cu(II) removal was more effective than at pH 2. Overall, it is evident that pH influences the heterogenization of Cu(II), even more the diversity of behaviors at different pH shows that the structural differences (crosslinking or active radicals) of PVP₂, PVP₂₅, and chitosan have high influence on the heterogenization. PVP₂ was the best material for the heterogenization of Cu(II) in acid media, it experienced a partial destruction and it was suggested a better exposure of pyridyl radicals. PVP₂₅ is suitable at variable pH, indicating that its structure was stronger than PVP₂ in acid media, similarly reported elsewhere [26]. Chitosan is more efficient near pH 5 due to its cationic adsorption increases at basic pH media as expected [27]. Finally, it was decided to develop the

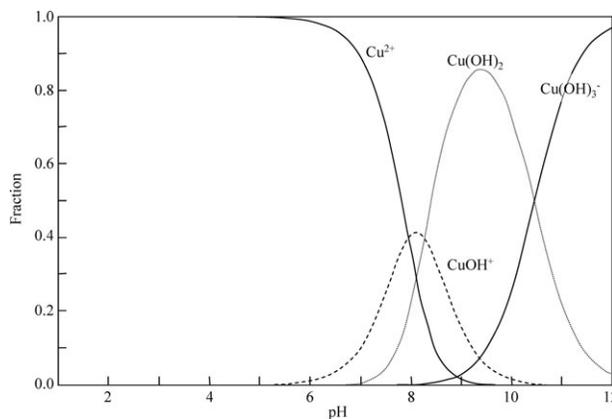


Figure 6. Distribution of Cu(II) species as a function of pH.

Table 1. Physical properties of polymers PVPs and chitosan.

Support	Particle size (mm)	Area BET (m ² g ⁻¹)	Average pore diameter (nm)	Adsorption capacity (mg g ⁻¹)
PVP ₂	~0.25	0.57	7.50	
PVP ₂ -Cu(II)		1.73	18.82	71
PVP ₂₅	~0.85	12.16	17.70	
PVP ₂₅ -Cu(II)		18.75	21.64	48
Chitosan*	~2.50	–	–	
Chitosan-Cu(II)*		–	–	10

*Difficult to be analyzed by standard methods because of its physical state of gel bead.

heterogenization of Cu(II) at pH 5 because, without pH control, the adsorption process does not present pH instability and because the catalyst was used at pH 6.

Effect of the Adsorbent on the Heterogenization

The uptake of Cu(II) was periodically evaluated, the initial copper concentration in solution was 1.0 g L⁻¹ for PVP₂ and PVP₂₅, for chitosan was 0.1 g L⁻¹ because initial experimental attempt demonstrated that chitosan presents low adsorption capacities. The experiments were carried out at the initial pH 5 and at the temperature of 20°C. The Cu(II) concentration in solution was monitored for 5 h, considering that all the adsorbent materials presented quite rapid adsorption rates at the first 2 h where equilibrium was reached, then adsorption contact time of 5 h was used for all further experiments. For instance, studies with chitosan have reported immediate adsorption uptake after 1 h [28].

From Table 1, it is evident the differences between the adsorption capacities of each support. Comparison between PVP₂ and PVP₂₅ showed that heterogenization of Cu(II) into materials with higher crosslinking had less adsorption capacities than their homologous with low crosslinking, even if they have higher BET area. Therefore, diversity of results was partially caused by the particle size of each material, because it was reported that adsorption capacity of materials with small particle size (e.g., PVP₂) were higher compared with beads [29]. For instance, beads (e.g., PVP₂₅ or chitosan) experiment obstruction problems in their contact area due to crosslinkage. A previous work described lower adsorption

capacity while the crosslinking increases [30]. Actually, the interaction between Cu and polymer is an important characteristic because while chitosan has $-\text{NH}_2$ radicals, PVPs have pyridyl radicals. Pyridyl group proved to be favorable for the adsorption of copper ions as this study shows [30]. Therefore, chitosan does not just present less adsorption capacities than the rest of polymers because of the external configuration (particle size) but also because of its amino radicals.

Effect of the Temperature on the Heterogenization

To study the influence of temperature over the heterogenization of the Cu(II) onto polymeric materials, it was schemed the adsorption capacity against the equilibrium concentrations of Cu(II) ions in solution at three different temperatures (20, 30, and 40°C).

Figure 7a shows the evolution of PVP₂ adsorption capacity (q) when temperature varies. PVP₂ with 2% of crosslinker presents high percent of ordered active radicals over its exposed area, but results show better q results with PVP₂₅ at 20°C (Figure 7b). PVP₂ shows saturation at 20°C but it seems to expose more amino radicals at 30 and 40°C. Then, the q of PVP₂ at 40°C (90 mg g⁻¹) and 30°C (71 mg g⁻¹) represent the equilibrium of an unsaturated material compared with the values obtained at 20°C (39 mg g⁻¹).

From PVP₂₅ (Figure 7b), it was deduced that PVP₂₅ performs a higher adsorption capacity than PVP₂ and chitosan at 20°C despite of its 25% of crosslinker. The adsorption capacity of PVP₂₅ decreases as effect of the temperature increment; for instance, there was no better adsorption activity at temperatures more than 40°C. Obviously, q was low because temperature increased the Cu(II) ions excitement, then the adsorption was hardly performed due to the attraction of Cu(II) to the polymeric surface is lower.

Previous reports have worked with chitosan in powder and flakes, from where it was obtained the highest q with powder materials at three tested temperatures [15, 29]. In Figure 7c, chitosan adsorption capacities kept constant even when temperature changed, characterizing chitosan as a polymer capable to attract the same amount of Cu(II) ions between 20 and 40°C. It was suggested that temperature could have more influence over Cu(II)-chitosan interaction if its adsorption capacities were higher.

Finally, given temperature has high influence over PVP₂ and PVP₂₅ adsorption capacities while had no effect on chitosan. It was confirmed that the exposed surface, which was formed by energy sites of available radicals, changed when temperature increased. Finally, it was established that temperature change has high influence on the heterogenization of copper [15].

Equilibrium Studies over the Heterogenization

Langmuir Study

The equilibrium data were analyzed by known adsorption isotherm models, which provided the basic theory in adsorption behavior. The Langmuir theory of 1916 [31], which follow the idea of a monolayer surface adsorption onto an ideal surface and was expressed by Eq. 2:

$$q = \frac{q_{\max} \cdot K \cdot C_e}{1 + K \cdot C_e} \quad (2)$$

where the adsorption capacity q (mg g⁻¹) is a function of Cu(II) concentration at the equilibrium C_e (mg L⁻¹), the Langmuir equilibrium constant K (L mg⁻¹) and the maximum adsorption capacity q_{\max} (mg g⁻¹). So that, linearization of Eq. 2 gives Eq. 3:

$$\frac{C_e}{q} = \frac{C_e}{q_{\max}} + \frac{1}{K \cdot q_{\max}} \quad (3)$$

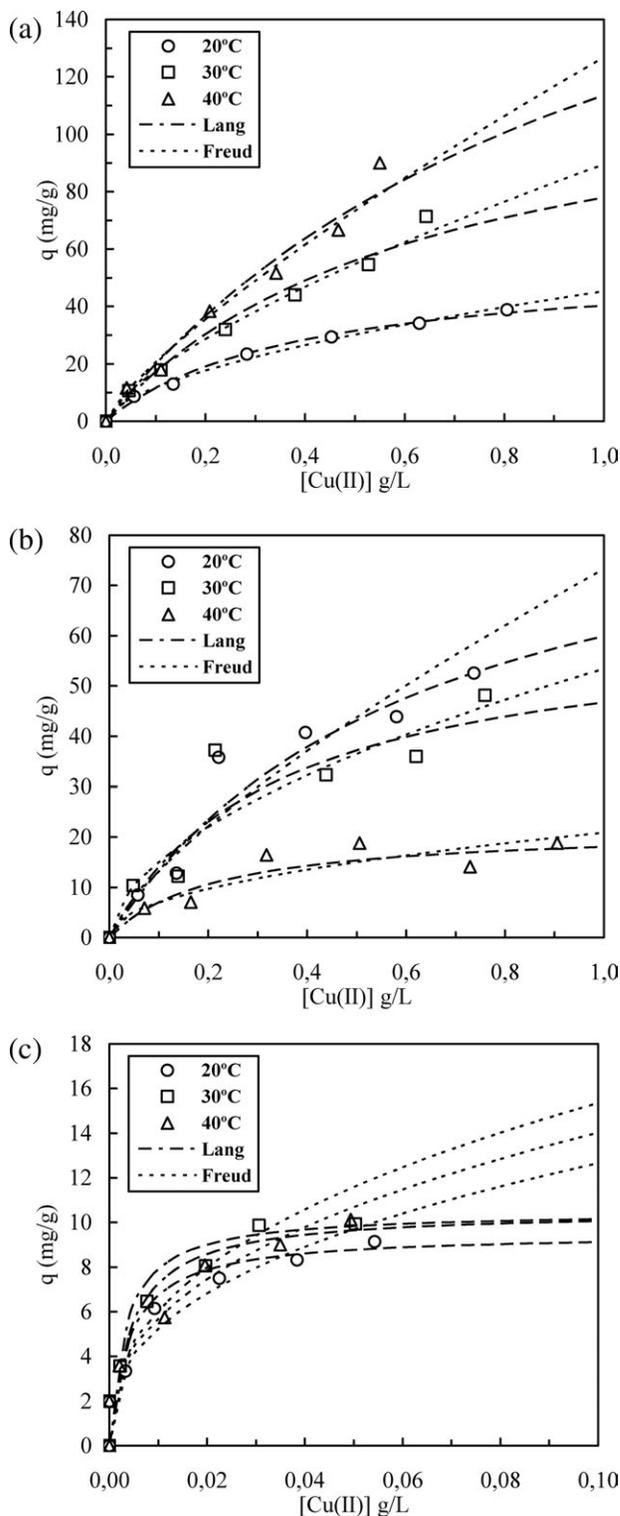


Figure 7. Adsorption isotherms of Cu(II) onto (a) PVP₂, (b) PVP₂₅, and (c) chitosan with their respective Langmuir and Freundlich evaluation at 20, 30, and 40°C. $[\text{Cu(II)}]_0 = 0.1\text{--}1.0 \text{ g L}^{-1}$ for (a) and (b), $[\text{Cu(II)}]_0 = 0.01\text{--}0.10 \text{ g L}^{-1}$ for (c), $m = 1$ g.

Langmuir constant K and q_{\max} were calculated from the plot of C_e/q vs. C_e . Then, on Table 2 Langmuir parameters were listed (K and q_{\max}) as indicators of the adsorption process. K represents the equilibrium constant and q_{\max}

Table 2. Langmuir parameters of Cu(II) adsorption onto PVP₂, PVP₂₅, and chitosan, $m = 1$ g at 20, 30, and 40°C.

Support	Temperature (°C)	K (L mg ⁻¹)	q_{\max} (mg g ⁻¹)	R^2
PVP ₂ (powder)	20	2.6×10^{-3}	56	0.9724
	30	1.5×10^{-3}	128	0.8356
	40	0.9×10^{-3}	238	0.4853
PVP ₂₅ (beads)	20	1.6×10^{-3}	98	0.7029
	30	2.9×10^{-3}	63	0.7478
	40	4.7×10^{-3}	22	0.8596
Chitosan (beads)	20	2.4×10^{-1}	10	0.9867
	30	3.1×10^{-1}	11	0.9880
	40	2.2×10^{-1}	11	0.9715

expresses the maximum adsorption capacity at monolayer levels [32].

PVP₂ case shows that K constant decreases when temperature increases, indicating the lack of saturation onto the sorbent surface at high temperatures and characterizing PVP₂ as a material with high adsorption capacities at high temperatures. For instance the highest q_{\max} value was obtained at 40°C where Cu(II) ions were well spread in the sorbet media, then the temperature facilitates the interaction of PVP₂ surface and Cu(II) ions.

Langmuir constants for PVP₂₅ (Table 2) show that K values increase with temperature and it describes high equilibrium constants at 30 and 40°C. It was observed a negative temperature effect over PVP₂₅ surface (reduction of adsorption capacity), that is the equilibrium constant increases because Cu(II) ions have difficulties to form bonds with the polymeric surface. Therefore PVP₂₅ has low q_{\max} values at high temperatures, which describes difficulties to form Cu(II)-polymer bonds at 40°C.

Likewise, chitosan Langmuir constants were presented on Table 2. K constant remains unchangeable at different temperatures. This behavior describes chitosan as a polymer capable to obtain equivalent adsorption capacities at different temperatures; in consequence, q_{\max} did not change at any tested temperature.

After Langmuir evaluation, PVP₂ presented the best energetic properties at monolayer coverage when compared with PVP₂₅ and chitosan, at this temperature range. Moreover, data were also evaluated by Freundlich model as follows.

Freundlich Study

Experimental data were analyzed by the Freundlich model [33], which assumes a heterogeneous surface with unequal adsorption sites and was expressed by Eq. 4 as a function of two constants called Freundlich K_f and $1/n$ parameters respectively:

$$q = K_f \cdot (C_e)^{1/n} \quad (4)$$

where K_f (mg g⁻¹) indicates the Freundlich adsorption coefficient of the polymer and $1/n$ (L g⁻¹) represents the adsorption intensity of formed bonds. For instance, n values between 1 and 10 range, it can be stated that the adsorption is favorable. The linearization of Eq. 4 gives Eq. 5:

$$\ln(q) = \ln(K_f) + \frac{1}{n} \cdot \ln(C_e) \quad (5)$$

After plotting Eq. 5, Freundlich constants were obtained and the results presented in Table 3. For PVP₂ case, K_f constant decreases with temperature; this effect shows less adsorbance affinity when temperature increased. Additionally,

Table 3. Freundlich parameters of Cu(II) adsorption onto PVP₂, PVP₂₅, and chitosan, $m = 1$ g at 20, 30, and 40°C.

Support	Temperature (°C)	$1/n$ (L g ⁻¹)	K_f (mg g ⁻¹)	R^2
PVP ₂ (powder)	20	0.58	0.80	0.9914
	30	0.71	0.67	0.9943
	40	0.79	0.54	0.9727
PVP ₂₅ (beads)	20	0.74	0.43	0.9059
	30	0.55	1.18	0.8001
	40	0.48	0.78	0.8055
Chitosan (beads)	20	0.38	2.16	0.9688
	30	0.41	2.36	0.9540
	40	0.39	2.30	0.9702

$1/n$ small values describe the strength of Cu(II)-polymer bonds, which in this case, increases with temperature, showing that the bond strength is weaker at high temperatures. Overall, PVP₂ presents better adsorption capacities at 40°C but at the same time its Cu(II)-polymer bonds lose strength.

Freundlich K_f parameter for PVP₂₅ does not present a tendency. K_f is nearly similar at 20 and 40°C, while K_f is almost the double than the previous temperatures at 30°C, this lack of tendency at different temperatures describes PVP₂₅ as an unsteady energetic surface. Moreover, the decrease of $1/n$ parameter represents the formation of stronger bonds, so that it was assumed that PVP₂₅ has stronger Cu(II)-polymer bonds when temperature increases.

From the evaluation of chitosan K_f and $1/n$ parameters, it was seen that these parameters are almost nonsensible respect to temperature such as the previous Langmuir evaluation. Moreover, chitosan data show the formation of strong bonds with the possibility to have better adsorption coefficients than PVP polymers.

Figures 7a and 7b plots Langmuir and Freundlich models for PVP₂ and PVP₂₅, respectively, the comparison between models showed that experimental data fitted either with Langmuir or Freundlich models. It was suggested that PVP₂ and PVP₂₅ have a homogeneous adsorption activity with an energetically heterogeneous surface. Figure 7c shows that Langmuir tendencies fitted well with the experimental data, describing chitosan as a support with a homogenous adsorption surface. This effect implies a well distribution of superficial energies, even when temperature increases.

Thermodynamic Study

Thermodynamic parameters describe the effect of temperature on Cu(II) heterogenization and evaluate the nature of the adsorption process. The thermodynamic constants, Gibbs free energy variation ΔG^0 (kJ mol⁻¹), enthalpy variation ΔH^0 (kJ mol⁻¹) and entropy variation ΔS^0 (kJ·mol⁻¹·K) were calculated. The Gibbs free energy change of adsorption was defined by Eq. 6:

$$\Delta G^0 = -RT \cdot \ln(K) \quad (6)$$

where K (L mol⁻¹) was taken from the evaluation of the Langmuir model and R is the Universal gas constant (8.314 J mol⁻¹ K⁻¹). The ΔG^0 values (Eq. 6) were listed in Table 4. The ΔG^0 negative values describe spontaneous adsorption processes for the four of the polymeric supports. Literature determines that ΔG^0 range from -8 to -6 kJ mol⁻¹ represents the bonding energy for an ion-exchange mechanism [34].

Note, for PVP₂, the increment of ΔG^0 implies less adsorption at high temperatures that is agreed with K Langmuir constant, which presented less bond affinity. Hence, PVP₂ adsorption capacity suggests a physical adsorption with a

Table 4. Thermodynamic sorption parameters of Cu(II) removal onto PVP₂, PVP₂₅, and chitosan, $m = 1$ g, at 20, 30, and 40°C.

Support	T	K (L mg ⁻¹)	ΔG^0 (kJ mol ⁻¹)	ΔH^0 (kJ mol ⁻¹)	ΔS^0 (kJ mol ⁻¹ K ⁻¹)
PVP ₂ (powder)	20°C	2.6×10^{-3}	-12.4	-40.5	-0.10
	30°C	1.5×10^{-3}	-11.5		
	40°C	0.9×10^{-3}	-10.5		
PVP ₂₅ (beads)	20°C	1.6×10^{-3}	-11.3	41.1	0.18
	30°C	2.9×10^{-3}	-13.1		
	40°C	4.7×10^{-3}	-14.8		
Chitosan (beads)	20°C	2.4×10^{-1}	-23.5	-3.1	-0.10
	30°C	3.1×10^{-1}	-24.9		
	40°C	2.2×10^{-1}	-24.9		

high desorption possibility. The ΔG^0 range (from -12.4 to -10.5 kJ mol⁻¹) indicates that PVP₂-Cu(II) bond was formed by electrostatic interactions between adsorption sites and Cu(II) ions, also called physical adsorption.

The ΔG^0 for PVP₂₅ shows an opposite behavior compared with PVP₂, it decreases with temperature increment. ΔG^0 values for PVP₂₅ are lower than PVP₂, but they suggest a feasible adsorption process promoted by low temperatures. The ΔG^0 range from -14.8 to -11.3 kJ mol⁻¹, near to -16 kJ mol⁻¹, describes the adsorption as a charge transference from the adsorbent surface to Cu(II) ions to form a coordinate bond such as previous experiences [35].

Heterogenization over chitosan did not vary with temperature. The ΔG^0 range from -24.9 to -23.5 kJ mol⁻¹ indicates that the ion exchange did not play a significant role in the adsorption process. Moreover, the interaction Cu(II)-chitosan involves a charge sharing from chitosan active radicals to Cu(II) ions. Additionally, thermodynamic potentials such as enthalpy ΔH^0 and entropy ΔS^0 variations were determined by Eq. 7 and evaluated.

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^0}{R \cdot T^2} \quad (7)$$

Equation 8 was obtained and ΔH^0 results categorize the adsorption as endothermic or exothermic heterogenization process and Eq. 9.

$$\ln(K) = -\frac{\Delta H^0}{R \cdot T} + \frac{\Delta S^0}{R} = -\frac{\Delta G^0}{R \cdot T} \quad (8)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

ΔH^0 and ΔS^0 parameters were taken from the Van't Hoff plots Eq. 9 showed on Figure 8, where ΔH^0 is the slope and ΔS^0 is the intercept (Eq. 9). The thermodynamic behavior of PVP₂ tends to decrease when temperature increases. Then, the adsorption capacity of PVP₂ is exothermic (-40.45 kJ mol⁻¹), also known as favorable heterogenization. However, PVP₂₅ presents an endothermic behavior, probably caused by the temperature increment [36]. The thermodynamic behavior of chitosan presents no changes either exothermic or endothermic at temperature variation. Then, chitosan has a constant adsorption activity at different temperatures.

Thermodynamically, the best adsorption system was based on high negative ΔH^0 values and high positive ΔS^0 values. But, in fact, the free energy must decrease to have a spontaneous adsorption and the variation of entropy should be negative to suggest a decreasing in the randomness at the solid/solution interface during the adsorption of Cu(II). Nevertheless, these standards were not always followed, for

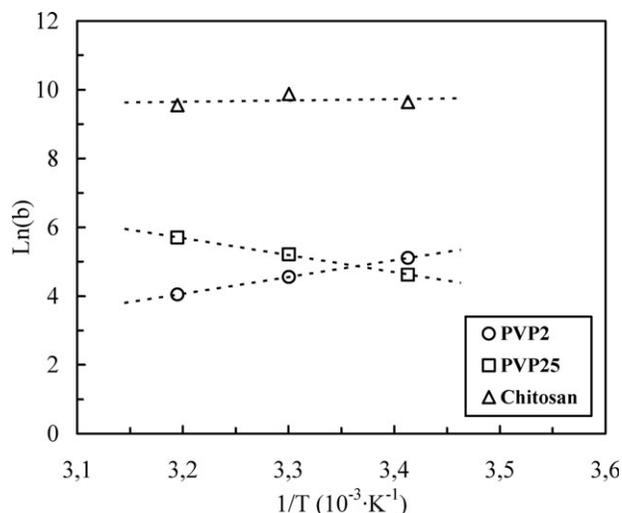


Figure 8. Van't Hoff diagram. Ln(b) versus T^{-1} . Thermodynamic tendencies of PVP₂, PVP₂₅, and chitosan. $[\text{Cu(II)}]_0 = 0.1\text{--}1.0$ g L⁻¹ for PVP₂ and PVP₂₅, $[\text{Cu(II)}]_0 = 0.01\text{--}0.10$ g L⁻¹ for chitosan, $m = 1$ g, $T = 20, 30,$ and 40°C .

instance it was reported that adsorption capacity for Cu(II) onto sand increased when temperature decreased [37], and studies of organic compounds adsorbed onto activated carbon also reported endothermic adsorption [36]. At the end, the ΔS^0 analysis describes the randomness degree of the adsorption process. For instance, PVP₂₅ adsorption presented a positive ΔS^0 value, which is a favorable degree of freedom expressed by randomness increment, also indicates that the adsorption leads to order through the formation of activated complex [27], suggesting that Cu(II) adsorption onto PVP₂₅ surface is an associated mechanism. However, PVP₂ and chitosan showed negative values, which usually reflects that no significant change occurs in the internal structure of the adsorbent during the adsorption process.

Kinetics of the Heterogenization of Cu(II) Catalysts

The adsorption data were used to examine the rate of the heterogenization process. Normally, the pseudo-first-order equation was expressed in the first contact time; on this period, the adsorption is highly favorable because the surface of the supports has great availability of energetic sites. The pseudo-first-order, generally applicable over the initial stage of adsorption processes, was based on the adsorption capacity and was expressed as (Eq. 10) [29]:

Table 5. Kinetic adsorption rate constant (k_1) and theoretical adsorption capacity (q_e^*) of Cu(II) onto PVP₂, PVP₂₅, chitosan. [Cu(II)]₀ = 0.1–1.0 g L⁻¹ for PVP₂ and PVP₂₅, [Cu(II)]₀ = 0.01–0.10 g L⁻¹ for chitosan, $m = 1$ g, $T = 20, 30,$ and 40°C .

Support	Temperature (°C)	k_1 (min ⁻¹)
PVP ₂	20	$2.3 \times 10^{-2} \pm 2 \times 10^{-3}$
	30	$1.2 \times 10^{-2} \pm 2 \times 10^{-3}$
	40	$0.9 \times 10^{-2} \pm 2 \times 10^{-3}$
PVP ₂₅	20	$2.6 \times 10^{-2} \pm 2 \times 10^{-3}$
	30	$1.1 \times 10^{-2} \pm 6 \times 10^{-3}$
	40	$0.8 \times 10^{-2} \pm 9 \times 10^{-3}$
Chitosan	20	$2.2 \times 10^{-2} \pm 2 \times 10^{-3}$
	30	$2.7 \times 10^{-2} \pm 4 \times 10^{-3}$
	40	$3.9 \times 10^{-2} \pm 5 \times 10^{-3}$

$$\frac{dq}{dt} = k_1 \cdot (q_e - q) \quad (10)$$

where the adsorption capacity (q_e) of the support at the equilibrium (mg g⁻¹) and the pseudo first-order rate k_1 constant (min⁻¹) were related, then Eq. 10 becomes into Eq. 11 [29]:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (11)$$

Additionally, for adsorption isotherms, it exist the possibility to follow the pseudo-second-order behavior, which was represented by two-step linear relationships [29].

Pseudo-first and second order models were applied; however, the three of the tested materials fitted well with the pseudo-first rate model. Table 5 lists the adsorption rate constants of PVP₂, PVP₂₅, and chitosan polymers, it is evident the increment of the constant rate for chitosan, while decreases for PVP₂ and PVP₂₅.

The decrease of the rate constant was due to the reduction of colliding molecules when temperature increases. For the case of chitosan with a slight increment on the constant rate when temperature increases, suggests that temperature promotes the entropy of the system with the excitement of Cu(II) ions, to finally increase the rate constant values.

Catalytic Testing of the Heterogeneous Cu(II) Catalysts

The catalytic oxidation of phenol was performed using PVP₂-Cu(II), PVP₂₅-Cu(II), and chitosan-Cu(II). The optimum catalyst was selected taking into account its catalytic activity in the reaction and its deactivation, mainly caused by the leaching of Cu(II).

Figure 9 shows the conversion of phenol and the leaching obtained along the reaction time at pH free. Figure 9a shows that PVP₂-Cu(II) and PVP₂₅-Cu(II) obtain the same 20% of conversion while chitosan-Cu(II) achieves 36%. From these results, the suitable catalyst for the process is chitosan-Cu(II); however, experimentally it was observed that chitosan was destroyed after 15 min, releasing its Cu(II) content to the reaction media, therefore being excluded as a suitable catalyst. The comparison between leaching of PVP₂-Cu(II) and PVP₂₅-Cu(II) demonstrated that PVP₂-Cu(II) had 5 mg L⁻¹ of leaching, which is an acceptable value for the pretreatments with metals [38]. As a result, PVP₂-Cu(II) was selected as the best catalyst for the oxidation of phenol at soft conditions.

Additionally and after the selection of PVP₂-Cu(II) as catalysts, it was evaluated the influence of temperature over the oxidation of phenol when using PVP₂-Cu(II) as catalyst. Three temperatures were tested (30, 40 and 50°C) and the pH was fixed to pH 6 to avoid Cu(II) leaching.

On Figure 10 was observed the results of phenol conversion, it is clear the influence of temperature over the reac-

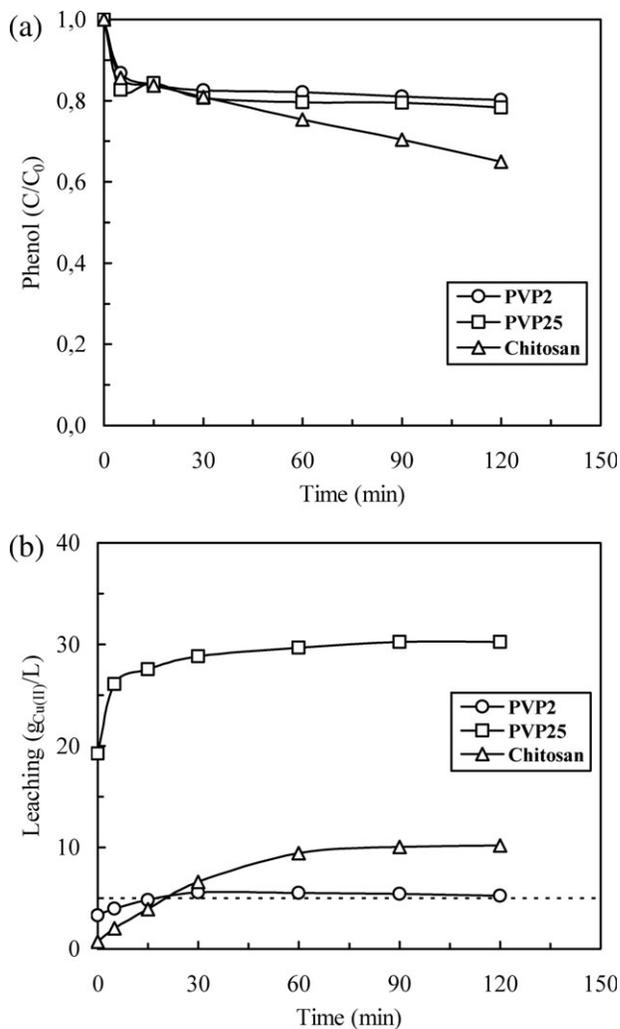


Figure 9. Heterogeneous catalytic phenol oxidation: Influence of the polymer-Cu(II) catalyst with the equivalent to 50 mg L⁻¹. (a) Phenol conversion and (b) Leaching. [Ph]₀ = 1 g L⁻¹, Ph:H₂O₂ 1:14 molar ratio, time = 2 h at free pH, 30°C and atmospheric pressure.

tion, up to 64% of phenol conversion at 50°C. Considering the metal leaching of the catalyst, it was observed that at pH 6 the leaching has decreased, but Cu(II) release at 50°C cross the limit (5 mg L⁻¹) of acceptable metal contamination for industrial effluents. Thereafter, it was suggested the use of PVP₂-Cu(II) as catalyst of the wet peroxide oxidation of phenol at pH 6, 40°C and atmospheric pressure.

CONCLUSIONS

The heterogenization of Cu(II) as catalyst for the oxidation of phenol was effectively conducted and the performances obtained are promising for its industrial utilization as pre-treatment for industrial wastewater. Among the polymer-Cu(II) catalyst tested, PVP₂-Cu(II) catalyst was selected as the most suitable catalyst for the process. This catalyst did not suffer destruction during the reaction period and its metal leaching was low and acceptable for the industrial wastewater (5 mg L⁻¹). The catalyst was tested at 40 and 50°C where phenol conversions up to 64% were obtained; however, it was recommended to work at 40°C to prevent leaching problems, allowing the possibility to work in continue and avoiding the necessity to remove the copper in solution.

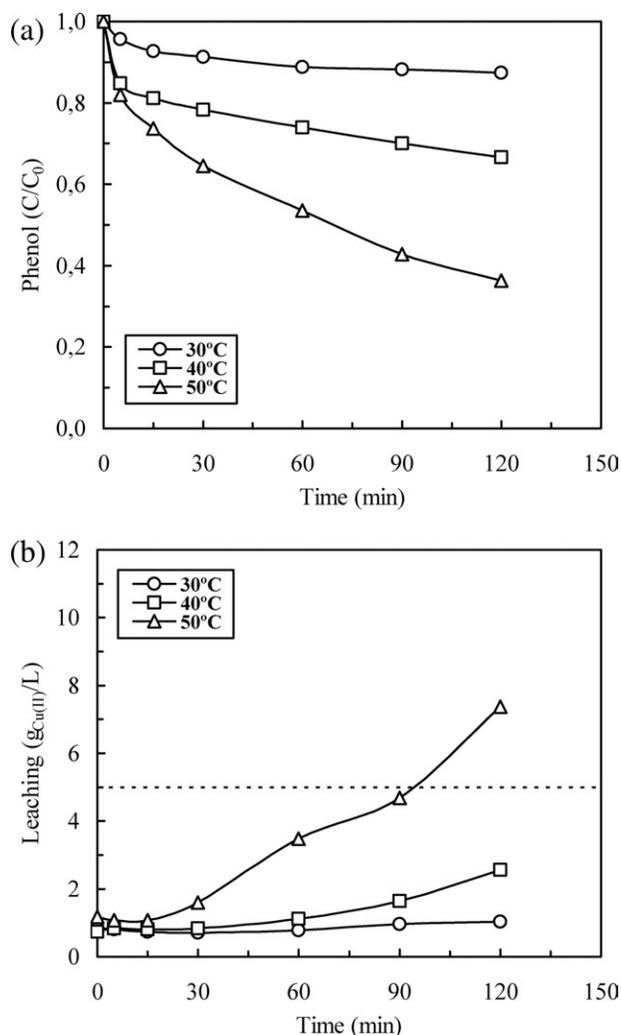


Figure 10. Heterogeneous catalytic phenol oxidation: Influence of the temperature (30, 40, and 50°C) when using PVP₂-Cu(II) as catalysts 0.45 g equivalent to 50 mg L⁻¹ of Cu(II) in solution. (a) Phenol conversion and (b) Leaching. [Ph]₀ = 1 g L⁻¹, Ph:H₂O₂ 1:14 molar ratio, time = 2 h at pH 6 and atmospheric pressure.

From the study of the properties of the catalysts, FTIR analysis described the differences between PVPs, where the crosslinking degree of polymers characterize their structural molecules and surface activity. The crosslinking degree, pH, and temperature influenced the heterogenization of Cu(II), especially for PVP₂ case. It has the lowest crosslinking degree and proved to get the highest q at acid pH and high temperatures, up to 90 mg g⁻¹ of Cu(II) at 40°C.

Langmuir and Freundlich models were applied to the experimental data to characterize the adsorption process. From these models, it was observed that the polymers under study present surfaces with different energetic and well organized areas where Cu(II) was attached. Even more, this behavior remains similar when temperature varied.

The kinetics of the heterogenization of Cu(II) describes the process by the pseudo-first rate model, which at the same time was recognized as a physisorption process. This type of adsorption highly impels the use of heterogeneous Cu(II) catalysts, on the oxidation of phenol, because the physisorption preserves the catalytic activity of the homogeneous Cu(II) catalyst in a heterogeneous form.

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