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Role of surface modification of some metal oxides with amino acids in upgrading the sonocatalytic degradation of nitrobenzene

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ABSTRACT

The influence of surface modification of some metal oxides (Fe_2O_3, CuO, NiO, and CO_3O_4) with amino acids was investigated in the sonocatalytic degradation of nitrobenzene (NB). Glycine, arginine, and glutamic acid were used as surface modifiers. This modification resulted in a considerable enhancement of sonochemical degradation of NB at pH higher than 7 with respect to the pristine catalysts before modification. Catalysts modified with arginine exhibited the highest degradation extent. The enhanced degradation efficiency was attributed to the promoted coupling via electrostatic attraction between the negatively charged NB molecules and the positively charged arginine layer on the surface of Fe_2O_3, CuO, NiO, and Co_3O_4. The attraction capability at all modified metal oxides increased via secondary forces such as hydrogen bonding, n–π and π–π interactions.

Keywords: Sonocatalysis; Nitrobenzene; Amino acid; Surface modification

1. Introduction

Nitroaromatics are common chemicals that are used in explosives, rocket fuels industries, dyes production, and also as intermediates of medicinal products [1,2]. These compounds can get into effluent waste and sewage in considerable amounts. They can also find a way easily into soil and groundwater thus, many problems exist, as these compounds are toxic and carcinogenic [3]. Over the last years, researchers have focused on finding effective degradation ways of these compounds [4,5]. Recently, chemical treatment methods, based on the generation of hydroxyl radicals, known as advanced oxidation processes (AOPs), have been applied for pollutant degradation, due to the high oxidative power of the OH radical. The most widely studied AOPs include; heterogeneous photocatalytic oxidation [6], treatment with ozone (often combined with H_2O_2, UVA, or both) [7–10], H_2O_2/UV systems [11], Fenton [12], and photo-Fenton type reactions [13].

Over the past several years, great attention has been paid to the use of ultrasound as one of the effective technologies for wastewater treatment [14,15]. Nucleation, growth, and finally, implosion of the cavities generated by ultrasound irradiation lead to extremely high local conditions of temperature and pressure which allow the formation of reactive radicals, such as $H^{\cdot}$, $HO^{\cdot}$, $O_2^{-\cdot}$, as well as the homolytic splitting of pollutant compounds. Degradation of pollutants using cavitation is based on the attack of the generated free radicals.

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On the other hand, ultrasonic irradiation generates benefits in heterogeneous catalytic systems by decreasing mass transfer limitations and fragmentation of catalyst in small particles that provide a higher surface area [16–21]. Moreover, the additional generation of free radical species in ultrasound systems should enhance the overall catalytic performance [19,22]. Thus, a combination of sonolysis and catalytic oxidation in one system helps to verify integration to the system thus, eliminates the disadvantages associated with each individual process [23,24]. The intensive chemical and energy inputs have the advantage to cause destruction of pollutants to acceptable degrees [25]. Sonolysis alone is not capable to fully degrade nitrobenzene (NB) as it is an extremely stable contaminant that can only be destroyed by vicious radical attack. It should also be noted that the use of a catalyst enhances the $OH^{\cdot}$ radical generation [26,27]. Hence, the combination is usually aimed to ensure higher degradation efficiency [28]. Gogate et al. [29] studied the sonophotochemical degradation of formic acid by the combination of ultrasonic irradiation and photocatalytic oxidation. Chakinala et al. [30] reported the use of a combination of hydrodynamic cavitation and heterogeneous advanced Fenton process for the treatment of real industrial wastewater. Pradhan and Gogate [31] studied the degradation of p-nitrophenol at pilot-scale operation by the combination of ultrasound-induced cavitational reactors and conventional or advanced Fenton process.

Continuous cleaning of the generated cavities on the catalyst surface is another advantage of the sonolysis application [16]. The cavitation threshold is lowered in the presence of trapped vapor–gas nuclei in the crevices of particulate material [32]. Therefore, the ultrasonic activation of the heterogeneous catalyst and/or lowering of the cavitation threshold might result in a synergism between ultrasonic irradiation and heterogeneous catalytic oxidation by H_2O_2 when both are applied simultaneously.

Huang et al. [33] studied the selective photoreduction of NB to aniline on TiO_2 nanoparticles modified with amino acid, or photocatalytic removal of nitroaromatics from wastewater, and found that the attraction capability was greatly increased at all modified TiO_2. The stronger attraction capability was attributed to hydrogen bonding, n–π and π–π interactions between modified TiO_2 and NB [33]. Similarly, specific reduction of 4-NP to 4-AP was achieved using arginine-modified TiO_2. Surface modification of TiO_2 with arginine changed the surface charge and resulted in enhanced reduction of 4-NP at pH 9, where the positively charged amine group on the side chain of arginine effectively complexes with negatively charged 4-NP. Photocatalytic reduction occurred specifically at aromatic nitro-groups and the half-wave reduction potential primarily governed the reaction rate [34].

In the current study, we combined sonolysis and catalysis by employing Fe_2O_3, CuO, NiO, and Co_3O_4 as heterogeneous catalysts at different pH values for degradation of NB. However, it was noticed from our previous study [35] that the degradation capability was greatly hindered at pH values >7 so we strongly believe that changing the surface nature of the catalysts by surface modification with a group of amino acids, that can render the modified surface acquiring different charge states, can be a good way to improve the degradation efficiency at pH >7.

2. Experimental

2.1. Materials

NB (99%), Glycine (99%), Glutamic acid (99%) were obtained from Sigma–Aldrich, and hydrogen peroxide (H_2O_2) (30% W/W), L-Arginine (99%) were purchased from Fluka (USA). Sodium hydroxide (96%), $FeCl_3{\cdot}6H_2O$, $COCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, and $CuCl_2{\cdot}2H_2O$ were purchased from Merck (Germany).

2.2. Preparation of surface-modified metal oxide catalysts

The catalysts precursors were prepared as described in our previous report [36]. The oxides were obtained after calcination in air at 450°C for 4 h. Then, a group of amino acids were used to modify the obtained metal oxides by soaking the prepared metal oxides in amino acid solution with weight ratio of metal oxide to amino acid (1:0.5, 1:1, and 1:2). Metal oxide MO (M = Fe or Cu or Ni or Co), was dispersed in a distilled water with a pH adjusted at 3.5, then an arginine solution (pH 11) was added slightly in excess of the amount required for monolayer surface coverage. Addition of arginine increased the solution pH to 9. The resulting suspension was stirred for 24 h at room temperature to ensure a complete complexation. The catalysts were isolated by filtration, washed several times with distilled water, and then exposed to drying in an evacuated desiccator. Once arginine was anchored to MO particles, it remained bound strongly. The glutamic-MO and glycine-MO catalysts were prepared by the same method as described above.

2.3. Characterizations

X-ray diffraction patterns were recorded in the range $2\theta = 4^\circ$–80°, using Philips Powder Diffractometer with Cu K_α radiation, which is operated at 40 kV at scanning speed of 2˚min^{-1}. FTIR spectra were obtained using ATI Mattson model Genesis Series (USA) infrared spectrophotometer adopting KBr technique.

2.4. Degradation of NB using ultrasonic irradiation

A commercial sonicator, VCX-750 (Sonics and Materials, Inc.) equipped with a titanium probe (diameter 13 mm) capable of operating continuously at a fixed frequency of 20 kHz with a variable electric output power up to 125 W was used for ultrasound experiments. Experiments were carried out in a glass reaction vessel with thin and indented bottoms for uniform and more efficient energy transmission. Ultrasound power output was set at 100 W for all the experiments. The reactor was assembled with the ultrasound apparatus and irradiated according to the experimental requires.

The actual power dissipated (P_{diss}) in the solution is not the same as the ultrasonic output power quoted by the manufacturer (P_{g}), due to the losses in the ultrasonic energy during the transfer processes. One of the most common methods of measuring P_{diss}, introduced by Lorimer et al. [37], is based on calorimetry and assumes that all the power entering the process vessel is dissipated as heat. Assuming 50 g water was used in the system, the value of P_{diss} was estimated to be 6.3 W. Ultrasonic density is the power supplied per unit volume of the medium, expressed as W/mL. The power density was found to be 0.126 W mL^{-1}.

The tip of the titanium probe was placed about 2 cm below the surface of the NB solution (10 mg L^{-1}) during sonication. During the degradation, the reactor temperature was thermostated at 25 ± 2˚C. The reaction temperature was monitored by a thermocouple located inside the reactor. The degradation of NB was initiated by rapid addition of the oxidizing agent (10 mmol L^{-1} of H_2O_2) to the reactor and immediately turning on the ultrasonic for 30 min. The reaction was quenched instantaneously by adding 2 g of $Na_2S_2O_3$ to the withdrawn samples (20 mL) before analysis. Aliquots were immediately centrifuged at 14,000 rpm for 15 min to remove the catalysts using EBA-21 centrifugal, Hettich-Germany. The resultant solution was used for the analysis of related chemical species in it.

2.5. Data collection and chemical analysis

The concentration of the undegraded NB was determined by solid-phase micro extraction using 65 um polydimethylsiloxane/divinylbenzene (PDMS/DVB) fibers (Sigma–Aldrich, Germany) in combination with GC analysis as described in our previous report [35]. Briefly, the fiber was introduced through the septum of a vial containing the solution withdrawn from the reaction flask and immersed in the solution for 30 min. During this time, the solution was stirred on a magnetic stirrer using glass-coated stirring bar. Afterward, the fiber was removed and introduced into the GC injector (220˚C 30 min, splitless injection) for desorption of analytes and GC analysis. The degradation of NB was monitored by determining the residual concentration remaining after certain periods of reaction using HP 5890 gas chromatograph, provided with a flame ionization detector and equipped with a column (3.048 m in length and 3 mm int. diam.) packed with Benton 34 (5%); diisodecyl phthalate 5% (wt%) on chromosorb W (AW) 80–100 mesh. The initial oven temperature (80˚C) held for 3 min, programmed at 2˚C min^{-1} to 120˚C (5 min). The injector and the detector temperatures were 250 and 275˚C, respectively. Under these conditions, the retention time for NB was 20.2 min.

3. Results and discussion

3.1. XRD and FTIR analysis of the catalysts

The XRD patterns of the prepared metal oxides are shown in Fig. 1. Comparing the characteristic diffraction peaks obtained for the catalysts with the corresponding ASTM cards revealed the formation of Fe_2O_3, CuO, NiO, and Co_3O_4 in a crystalline form.

The FTIR spectra of the different catalysts before and after treatment with different amino acids are shown in Figs. 2 and 3. The FTIR spectrum of the different catalysts before treatment contains absorption bands appearing around 500 $\mathrm{cm}^{-1,}$ which are characteristics for the metal oxides as shown in Fig. 2 while after performing the treatment with arginine as shown in Fig. 3, the appearance of new absorption bands pertaining to the existence of the amino acids modifier on the surface of the inorganic catalysts can be easily

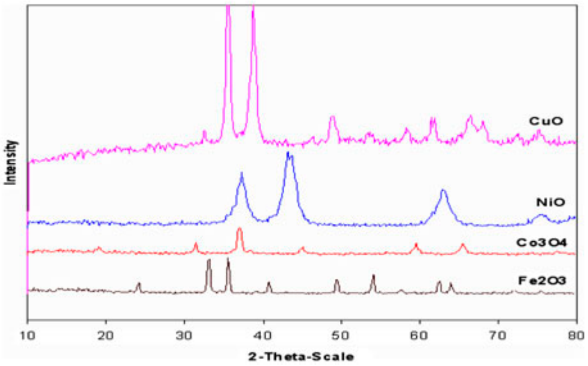

Fig. 1. XRD patterns of Fe_2O_3, CuO, NiO, and Co_3O_4.

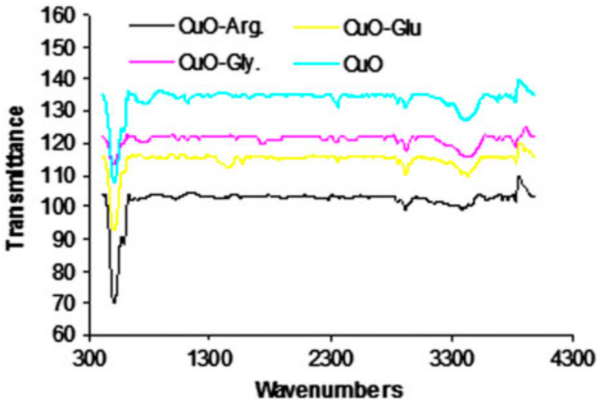

Fig. 2. FTIR spectra of CuO catalysts before and after modification with different amino acids.

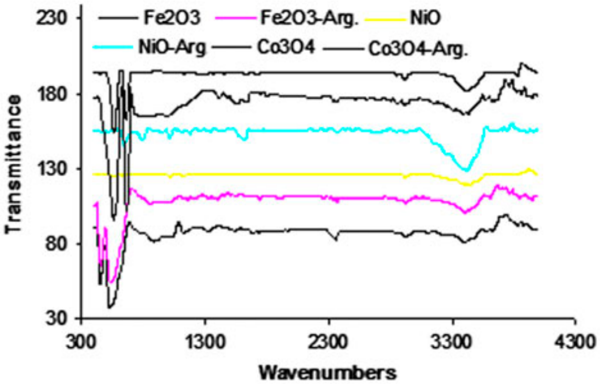

Fig. 3. FTIR spectra of different catalysts modified with arginine.

recognized, for example, the absorption bands at 2,900–2,920 cm^{-1} that belong to CH_2 aliphatic along with the absorption band belonging to $–NH_2$ groups at 3,400 cm^{-1} [38]. Additionally, the carbonyl absorption bands appear obviously at 1,625 cm^{-1} (CuO, Fig. 2), 1,611 cm^{-1} (NiO, Fig. 3) and much less intense in the other cases.

3.2. Sonocatalytic degradation of NB assisted with H_2O_2 solely

The effect of different pH values on the degradation of NB is presented in Fig. 4. The experimental results reveal that the sonocatalytic degradation extent decreases with the increase of the solution pH as shown in Fig. 4. At higher pH values, H_2O_2 is decomposed into H_2O and O_2. Hydrogen peroxide is one of the active components in the system, responsible for generating $OH^{\cdot}$ radicals that will be subsequently consumed in inducing degradation of NB. Thus, its decomposition at pH values 9–11 necessarily means that the production of the degradation dependent $OH^{\cdot}$ species will be slowed down [39].

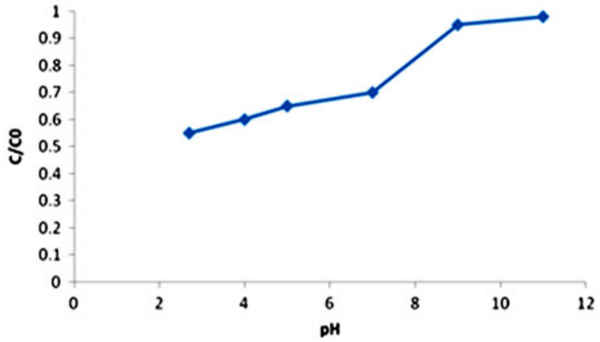

Fig. 4. Degradation of NB at different pH values performed with assistance of 10 mM H_2O_2 and sonication for 30 min.

3.3. Sonocatalytic degradation of NB using metal oxide catalysts (before modification) assisted with H_2O_2

The degradation of NB was carried out at different pH value in the presence of metal oxide catalyst (1 g L^{-1}), (Fe_2O_3, CuO, NiO, Co_3O_4) using 10 mM H_2O_2 while the ultrasonic was operated continuously for a period of 30 min. Fig. 5 represents the degradation profiles obtained under the catalytic effect of the catalysts in combination with ultrasonication power. The results reveal that all the catalysts acquired the same trend and behaved monotonically. The maximum activity for degradation was achieved at pH range 5–7 then it decreased significantly at higher pH values. In the case of CuO (Fig. 5), the degradation efficiency of NB after 30 min reached 30% at pH 9 and 20% at pH 11. However, generally, the catalysts activity under these conditions can be arranged in the following order: $Fe_2O_3 > NiO > Co_3O_4 > CuO$ at pH range 9–11

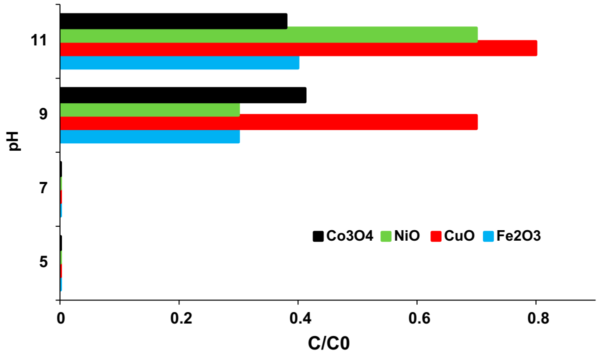

Fig. 5. Degradation of NB at different pH values performed with assistance of 10 mM H_2O_2 in the presence of different metal oxides as catalysts (1 g L^{-1}) and sonication for 30 min.

while at the lower pH range their potential in enhancing the NB degradation was almost the same (maximum activity). Furthermore, the metal oxides as an active forms could be converted to a much less active hydroxyl form, which decreases the electrostatic attraction of the NB on its surface, possibly, because the metal hydroxide surface species would form on the metal surface when NaOH was added into the reaction solution [40]. Moreover, it is known that the degradation of any pollutant occurs favorably at a specific pH range, at which the catalyst acquires a charge state opposite to the pollutant charge, thus, leads to electrostatic attraction, which enhances the degradation process [41]. Under strongly alkaline conditions, because of the repulsion force due to the negatively charged surface, the NB anions in aqueous solution are mainly degraded through radical ($OH^{\cdot}$) oxidation in bulk solution which is a slow degradation process because it is controlled by the diffusion of the radicals toward the bulk of solution, and of low efficiency due to the fast decomposition of H_2O_2 into H_2O and O_2 at strong basic conditions. On increasing the solution pH, the NB anionic form dominates with a consequent increase in hydrophilicity making the reaction with hydroxyl radicals to take place to a large extent in the liquid bulk resulting in reduced extent of removal possibly due to the presence of less hydroxyl radicals in the liquid bulk as compared to the site of cavitating bubble or the bubble–water interface.

3.4. Sonocatalytic degradation of NB using amino acids—modified metal oxides assisted with H_2O_2

The modified catalysts were tested in the degradation of NB in comparison with those untreated. The results of the degradation studies are shown in Figs. 6 and 7.

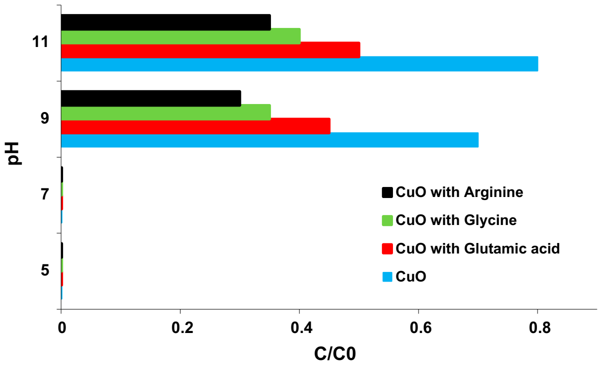

Fig. 6. Degradation efficiency of CuO as a catalyst modified with different types of amino acids ($1\,g\,L^{-1}$) in the presence of 10 mM H_2O_2 and sonication for 30 min.

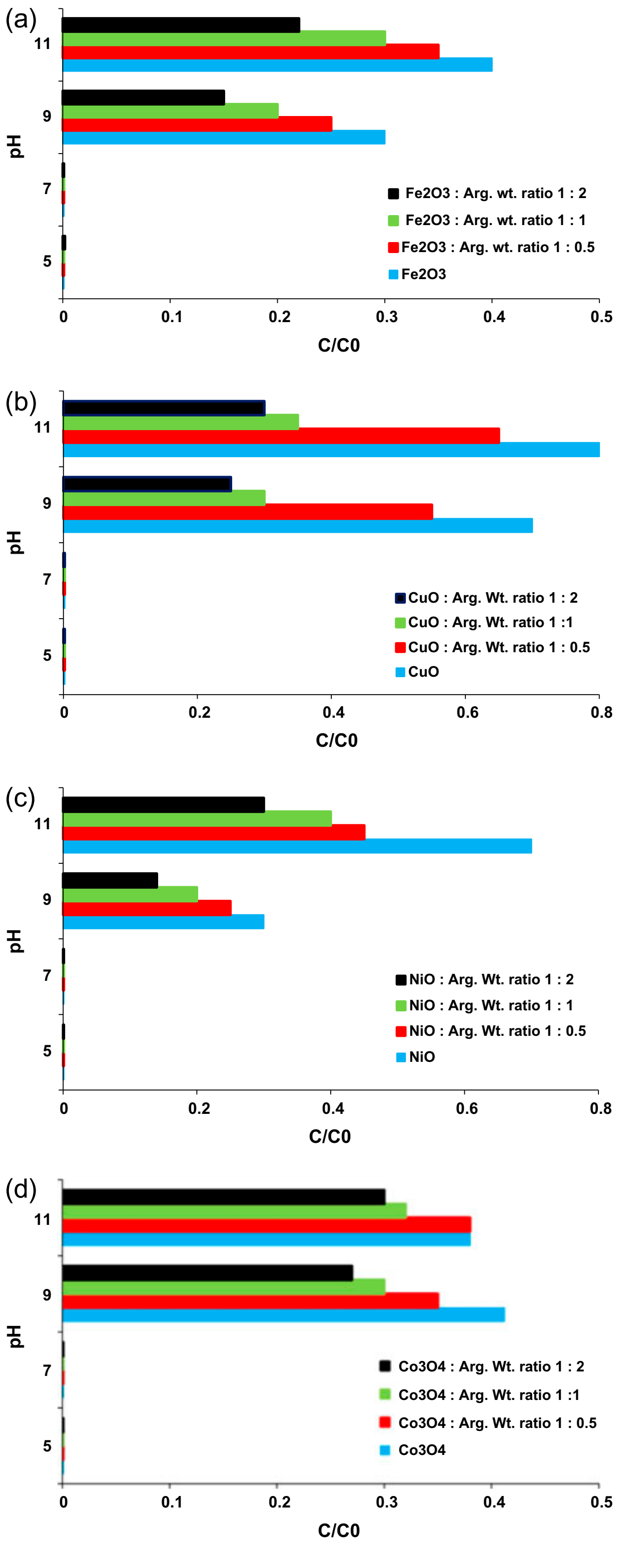

Fig. 7. Degradation efficiency of different catalysts modified with different concentrations of arginine ($1\,g\,L^{-1}$) in the presence of 10 mM H_2O_2 and sonication for 30 min, (a) Fe_2O_3, (b) CuO, (c) NiO, and (d) Co_3O_4.

In preliminary mapping experiments, we used CuO as a catalyst, modified with glutamic acid, glycine, and arginine, respectively. The modified catalysts were tested at the pH range that showed dormant activity (pH 9–11). Arginine exhibited the best catalytic activity over the other modifiers as shown in Fig. 6. Consequently, arginine was used as a modifier for the rest of the catalysts at different extents as shown in Fig. 7. From the figures, it turn out that for a given modifier (arginine), the activity of the catalysts can be arranged according to the following order $Fe_2O_3 > NiO > Co_3O_4 > CuO$ with a weight ratio of metal oxide to arginine (1:2). The results show that the degradation efficiency decreases with the decrease in the concentration of amino acid modifier, as shown in Fig. 7. This reveals that the acquired activity is referring to the amino acids, which have some catalytic role in promoting the NB degradation. Liedberg et al. [42] conducted similar modification on the Cu surface using L-histidine and L-phenylalanine and reported that the surface binding is attributed to ligand exchange reactions; $–NH_2$ and –COO groups replace surface hydroxyls or oxygen ions forming $Cu–NH_2$ and $Cu–COO^-$ bonds, respectively. However, Schmidt and Steinemann [43] reported that the modification using several amino acids adsorbed on TiO_2 surfaces is attributed to a ligand exchange reaction by which only –COO groups replace surface hydroxyls. In addition, Ahn et al. [34] studied the degradation of 4-NP using TiO_2 modified with arginine. They reported that the modification treatment with arginine created a positive charge on TiO_2 surface, over a wide range of pH values, which improved the attraction of NB on the surface. As a result, the degradation rate of 4-NP increased remarkably at high pH values.

It is to be noted that leaching of used oxides was tested by tracing the soluble species at the end of the experiments. It has been found that the concentrations of different ions were under the limits of detection which indicates that the participation of homogeneous Fenton is practically absent.

3.5. The influence of coupling interactions of amino acids with catalysts surface

The experimental results reveal that the sonocatalytic degradation extent decreases with the increase of the solution pH as shown in Fig. 5, which is attributed to the repulsion between the negative metal oxide surface and the negatively charged NB, decreasing the number of active sites for NB and finally, decreasing the degradation extent of NB. However, the modification of metal oxide surface with arginine inverts the surface charge from negative to positive thus eliminating electrostatic repulsion of NB at higher pH value.

Furthermore, the point of zero charge of Fe_2O_3, CuO, Co_3O_4, and NiO is 8.5, 8.4, 8, and 8.6, respectively. Above this pH value, the surfaces of these particles are negatively charged, while below this pH value they are positively charged. If arginine attached to the metal oxide surface is assumed to have the same pKa values as free arginine, the terminal amine group at the end of arginine's side chain is expected to be protonated, carrying a positive charge for pH values below 11 [34].

So in order to let the arginine strongly bound to the surface of the metal, we adjusted the solution pH at 9 during the preparation of the arginine-modified metal oxide. At this pH, the metal oxide surface is negatively charged while the net charge of the arginine is positive. The pKa of NB is 3.98; therefore, on increasing the solution pH the anionic form dominates [36]. Thus, during the degradation process at pH 9, it is expected that the negatively charged NB will be strongly attracted to the arginine-modified metal oxide which means that NB will be subjected to the higher number of generated $OH^\cdot$ radicals on the surface of the metal oxide, as a result the degradation was promoted.

At pH 11, significant decrease in NB degradation is clearly noted as shown in Fig. 7 because arginine is neutral and the negative metal oxide surface acts to repel the negatively charged NB.

It was found that the attraction capability was greatly increased at all modified metal oxides, which reflects that the binding of the pollutant can take place via other secondary forces such as hydrogen bonding and van der Waals interactions [33], which highlights the enhanced coupling between NB molecules and arginine at these pH values even in the presence of strong electrostatic repulsive forces. This can be accounted for the predominance of other stronger attraction capability like hydrogen bonding, $n–\pi$ and $\pi–\pi$ interactions [44,45].

It is to be noted that 10 mM H_2O_2 is greater than the stoichiometric concentration needed to complete mineralization of $10\,mg\,L^{-1}$ of NB. It is also expected that there will be other intermediates such as polyhydroxy benzenes, nitro phenols, etc. along with nitrite and nitrate ions present during the degradation. Some other aliphatic compounds may also be present which on reaction with hydroxyl radicals will be mineralized to CO_2 and H_2O according to literature [46]. We were not able to identify any known intermediates or by-product to the reaction of hydroxyl radicals with NB. However, we suggest that as long as the concentration of H_2O_2 is greater than the stoichiometric concentration for complete mineralization, the reaction has passed through hydroxylation followed by ring opening, and then finally mineralization.

4. Conclusions

The catalytic efficiency of some catalysts supported by sonolysis can be markedly promoted through surface modification using some modifiers such as amino acids to change the surface charge from net negative to net positive, which enhanced the degradation efficiency of NB at pH higher than 7, where the positively charged amine group on the side chain of arginine effectively complexes with negatively charged NB via electrostatic attraction, thus, NB will be subjected to the higher number of generated $OH^{\cdot}$ radicals on the surface of the metal oxide, accordingly increases the degradation efficiency.

Acknowledgments

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