

Sol-Gel Derived Ormosil-Exfoliated Graphite–TiO₂ Composite Floating Catalyst: Photodeposition of Copper

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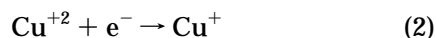
A new class of floating photocatalyst that can be used for recovery of copper from aqueous solutions is reported. The photocatalyst is comprised of a dispersion of titania nanocrystals in exfoliated graphite using organically modified silicate (Ormosil) as a binder. The composite materials were prepared by a two-step acid-catalyzed sol–gel preparation protocol. The efficiency of copper recovery under UV irradiation is compared for the floating catalysts, nanocrystalline titania suspension, and titania films. The floating catalyst could be used for prolonged duration, showed good regeneration capability and considerable amount of the recovered copper “peeled off” in metallic form, and could be in solid form without further acid redissolution.

Introduction

Semiconductor-based photocatalysis has been a subject of numerous investigations.^{1–3} In the past decade the interest in titania-based photocatalysis for a cleaner environment has attracted considerable attention particularly for the degradation of organic pollutants^{5,6} and metal recovery.⁷ The pioneering report of Wrighton and co-workers⁸ on deposition of copper on SrTiO₃/TiO₂ electrodes and the work of Reiche and Bard^{7a} on photodeposition of copper using titania suspension initiated photochemical⁹ and photoelectrochemical¹⁰ studies on the photodeposition of metals on titania and other semiconductive materials. Initially, photodegradation and photodeposition of metals on semiconducting photocatalyst utilized titania only in the form of aqueous suspen-

sion^{11,12} and thin films,¹³ but recently, floating catalysts in the form of coated glass beads,¹⁴ titania aerogels,¹⁵ and Ormosil–titania¹⁶ composites were introduced for photooxidation of organic pollutants. Floating catalysts are especially useful means for efficient utilization of solar radiation.

In this report, the application of a new composite floating catalyst comprised of expanded graphite, nanocrystalline titania (Degussa, P-25), and sol–gel derived organically modified silicate binder for photodeposition of copper is reported. The versatile method of preparation of the catalyst, its high stability, and its ability to sustain reactivity and floatability after repeated deposition–regeneration cycles are illustrated. The performance of the catalyst is compared to titania catalyst in the form of suspension and film. Copper recovery was chosen as a test case due to the large losses of copper in metal finishing and electroplating industries (for example, the annual consumption of copper in the United States alone is approximately 2.5 megatons)^{9a} and the fact that its photorecovery by titania and particularly P-25 catalyst is well documented.^{9a} In general, conversion of Cu²⁺ ions to Cu⁰ on illuminated titania particle obeys the following equations:^{7a}



The relevant standard potentials at pH 0 are 0.15, 0.52,

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and -0.2 V/NHE for eqs 2, 3, and the conduction band electrons, respectively.^{9a} Deposition of the copper is not limited to the surface of the titania. The conduction band electrons can be transported to the deposited copper inducing further copper reduction and deposition on the metal surface. The hole is scavenged by water to form a highly reactive hydroxyl radical ($E^\circ = 2.8$ V/NHE) or by a potent, sacrificial reducing agent such as, 2-propanol, citric acid, or other organic compounds.

Experimental Section

Preparation of the Buoyant Photocatalysts. Floating catalyst was prepared by coating exfoliated graphite (EG) particles with titania, P-25 using sol-gel derived methyl silicate binder according to ref 17. EG was prepared by thermal exfoliation of intercalated graphite compound (bisulfate graphite, Asbury Graphite Co.). Exfoliation of the graphite was carried out by heating to 1000°C for 20 s. The graphite produced had a bulk density of 5 g L^{-1} , residue ash content of 0.1%, particle size distribution of 0.2 mm (approximately 70%) and $20\text{ m}^2\text{ g}^{-1}$ N_2 BET surface area with 10–15% volume of closed pore.¹⁷

The coating procedure was as follows: 10 mL of methanol, 80 mg of titania, P-25, and 100 mg of methyltrimethoxysilane (MTMOS) were mixed in a 20 mL vial and sonicated for 15 min, to ensure uniform dispersion of titania. EG (100 mg) was subsequently added to the mixture and shaken for 5 min. Then, 0.1 mL of 1 N HCl was added to hydrolyze the MTMOS (water to Si ratio, $r = 7.5$). The mixture was allowed to hydrolyze for 3 h in a closed vessel and poured in a plastic Petri dish for drying. The contents of the Petri dish were constantly mixed for uniform distribution of titania in the EG. The color of the catalyst changed from black to gray during the preparation. After drying at room temperature for 24 h, the floating catalyst was incubated at 90°C for 24 h to remove residual methanol. At high titania concentration (>85 mg of titania/100 mg of graphite) the titania tended to aggregate and had to be separated mechanically.

Preparation of Supported Titania Films. Titania films were prepared by repeated dip coating of glass slides with a titania P-25 suspension using sol-gel derived methyl silicate binder. The glass slides were degreased in methanol and chromic acid and air-dried before use. The coating sol contained 10 mL of methanol, 80 mg of titania, P-25, 100 mg of MTMOS (Aldrich) and 0.1 mL of 1 N HCl providing a (molar) water to Si ratio of 7.5:1. Prior to coating, the sol was allowed to age for 3 h in a closed vessel. After each dipping step the coated films were dried at 80°C for 1 min. The films had a thickness of less than $10\ \mu\text{m}$, as deduced from the penetration of the beam during EDS analysis. In addition all the incident light was absorbed by the film, and thereby a further increase in thickness had no effect on the photocatalytic activity of the film. The method is similar to that used by Heller and co-workers for the preparation of titania-modified hollow glass beads.^{6a}

The photolysis of copper ions on the surface of the floating catalyst was carried out in a cylindrical Teflon cell (15 cm^3) with a 9.62 cm^2 quartz window (10 mm thick) for illumination from top. Sampling was performed using a microsyringe (Hamilton) through a 1 mm in diameter sampling port sealed with a rubber septum.

The 15 mL volume of the cell was filled with an acidified (0.1 M H_2SO_4) solution of 0.1 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The solution was continuously stirred and deaerated by purging of N_2 gas (99% pure) for 30 min prior to the photodeposition test. Triply distilled water ($<1\ \mu\text{S}$ conductivity) was used in all experiments. The photocatalyst was titania, P-25 from Degussa which was introduced into the cell as a sonicated suspension, as a titania-coated glass slide, or as a layer of floating catalyst. The amount of floating catalyst and the thickness of the coated

film was sufficient to absorb all useful light, so that further increase in film thickness or titania concentration did not result in a further increase in the rate of copper deposition. The initial pH of the solution was 1.6 for all experiments, and varied between 0.5 and 4.22 by addition of sulfuric acid (96.6%, J.T. Baker) for studies on effect of pH on copper deposition. Unless otherwise stated, the illuminated cell was held at a constant temperature of 25°C and for investigations on the effect of temperature, it was varied between 10 and 50°C by circulating water through a regulated thermostat.

The irradiation was carried out using a 300 W Xe lamp (ozone free) from Oriol. The lamp housing was equipped with a dichroic mirror which reflected light in the wavelength region 280–400 nm. The wavelength greater than 400 nm was not reflected onto the cell. Unless otherwise stated, the light intensities reported in this article refer to the total flux between 280 and 400 nm, which is the useful flux capable of exciting the valence band electrons of titania. The intensity of photons hitting the quartz window was adjusted by using a thermopile light intensity monitor, Ophir, Nova 03A-P-CAL (Jerusalem, Israel). The light flux was varied from 15 to 225 mW cm^{-2} by adjusting the distance/focus of the beam.

During the course of the experiment the depletion in the concentration of Cu^{2+} ions in solution was monitored by the change in the absorption of the 808 nm peak of Cu^{2+} on a Varian, Cary 1E UV-vis spectrophotometer. Copper concentrations in the range 50–700 μM were monitored using an atomic absorption spectrophotometer (Perkin-Elmer 5000), and larger copper concentrations were measured by monitoring the absorbance at 435 nm of the Cu^+ -*o*-phenanthroline complex.¹⁸ Scanning electron microscope (SEM) studies and electron probe analysis were conducted using a JEOL 840 microscope. Energy-dispersive spectra (EDS) was taken on a Link 10000, calibrated with cobalt, and operated at 20 kV.

Results and Discussion

Figure 1A shows the secondary emission image (SEI) of a floating catalyst (composition: TiO_2 :Ormosil:EG = 0.8:1:1). The titania crystals are the white sites and the gray/dark regions are ascribed to the bare EG or to pores on the EG, as confirmed by elemental analysis. On illumination of the catalyst in the presence of Cu^{2+} ions (Figure 1B) the surface becomes less fibrillar and more granular in nature. Metal crystals of 10–15 μm can be clearly seen on the surface of the catalyst surrounded by smaller, 1–5 μm crystallites of copper. Figure 1C shows a magnified view ($4000\times$) of a single prismatic crystal of copper approximately 15 μm in diameter formed on the surface of the floating catalyst. The morphology of the crystals can be compared to the copper deposit on titania film which is considerably smaller and much less homogeneous in size (Figure 1D). In the case of copper-deposited titania suspension, although the copper covered 93% of the titania surface (Table 1), the morphology of the copper crystals was not well defined (Figure 1E). A possible reason for the different morphology of the deposit on the floating photocatalyst is that the rougher surface of the floating photocatalyst gives much larger free volume for growth of copper particle per nucleation site as compared to the planar configuration of the film. The titania colloids, on the other hand, cannot support large copper crystals.

The existence of preferential sites for copper nucleation and deposition is also apparent from the surface elemental analysis studies summarized in Table 1. Before the illumination the plate consisted of 91% titania and 9% SiO_2 , and after 1.4 mg of copper was

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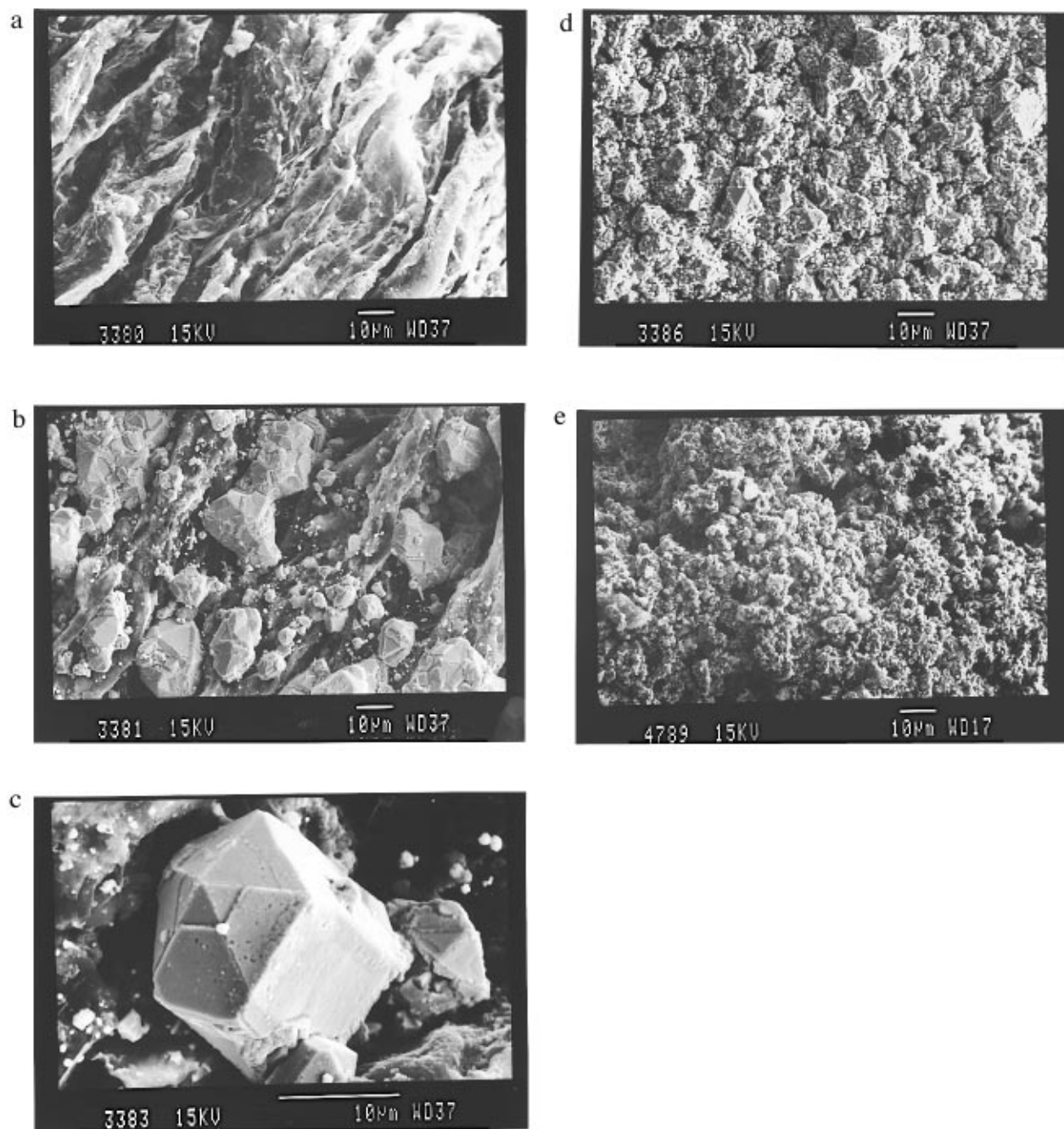


Figure 1. (A) SEI of floating catalyst containing 80 mg of titania P-25, in 100 mg of EG bound by methyl silicate binder; (B) SEI of copper deposited on floating catalyst after 56 h of illumination at 225 mW cm^{-2} using a Xe lamp from a solution containing 0.1 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 0.1 M 2-propanol in 0.1 M H_2SO_4 ; (C) SEI of a single crystal of copper on the surface of the floating catalyst; (D) SEI of copper deposited on the surface of titania-coated plate (6.25 cm^2); (E) SEI of titania powder after copper deposition.

deposited on the film 85% of the surface was covered by the copper metal. In comparison, after deposition of 3 times this amount of copper (4.2 mg) on the floating catalyst (covering the same cross-sectional area) the copper occupied only 45% of the outer surface of the floating catalyst. This is commensurate with the fact that the copper crystals are much larger and thus cover a significantly smaller surface area. Additionally, Table 1 suggests that a considerable amount of the copper is deposited on the carbon and not on the titania because after copper deposition the area occupied by titania and silica was reduced from 37% to 17% (i.e., 20% reduction) while the surface coverage by copper was more than twice larger (45%).

In both the plate and the floating catalyst a considerable amount of the copper deposit was peeled off and could be accumulated without redissolution in acid. Table 2 describes the distribution of the copper between the deposited phase on the photocatalyst and the peeled off metal. 25% of the copper deposited on the plate was peeled off, and 16% of the copper reduced by the floating photocatalyst was peeled off. In both cases the percentage of titania in the peeled off material was less than 0.5%. The peeled off copper can be directly used as a relatively pure metal, while in the case of the suspension it is impossible to separate the copper from the titania particles, without further acid or air oxidation.

Table 1. EDS Elemental Analysis of Photocatalysts^a

catalyst configuration	Cu	SiO ₂	TiO ₂
plate before Cu deposition	0%	8.8%	91.1%
plate after Cu deposition	86%	0.3%	0.8%
composite catalyst (TiO ₂ :Ormosil:EG = 0.8:1:1) before Cu deposition	0%	24%	13%
composite catalyst (TiO ₂ :Ormosil:EG = 0.8:1:1) after Cu deposition	45%	13%	3.8%
titanium P-25 suspension	0%	0%	100%
titanium suspension after Cu deposition	93%	0%	7.1%
peeled off Cu from the composite catalyst	99.7%	0%	0.28%
peeled off Cu from titania film	99.4%	0%	0.5%

^a EDS data were not normalized to 100%; the residual reflects the inaccuracy of the method and the contribution of carbon.

Table 2. Distribution of Copper after Deposition

catalyst	bound Cu (mg cm ⁻²)	free Cu (mg cm ⁻²)
suspension	0.35	<i>a</i>
plate	1.04	0.36
floating catalyst	3.79	0.57

^a The free Cu could not be separated from the Cu bound to the titania particles in suspension.

Kinetics of the Deposition Process. Figure 2 shows seven successive cycles of photodeposition of copper on titania P-25 suspension, titania-coated plate, and floating catalyst. The duration of each cycle was 480 min, and the starting concentration of 0.1 M was allowed to decay approximately 70% of the initial od value, and then the concentration of the copper was increased again to its original concentration without acid regeneration of the photocatalyst. The process follows zero-order kinetics for all three configurations of catalysts at high CuSO₄ concentrations with quantum yield = 0.7%. First-order kinetics (correlation coefficient, *R* = 0.98; relative standard deviation, RSD in slope = 10%) is obeyed at low copper concentration (<0.5 mM). This was independently confirmed by determining the rate constant using copper concentration of 0.5 mM (Figure 3).

An initial, slow deposition period is observed for all three catalysts only in the first cycle. The initial slow deposition rate of the freshly prepared particles may be attributed to their initial hydrophobicity. The illumination oxidized some of the methylsiloxane groups close to the titania active site, thereby reducing the hydrophobicity. The lag phase could also be attributed to the conversion of Cu(II) to Cu(I) which gives a purple Cu–TiO₂ species, prior to reduction of Cu(I) to Cu(0).^{9a}

The variations in the first-order rate constant for the floating catalyst, plate, and suspension per unit surface area of illumination are summarized in Figure 4. The profile clearly indicates that the performance of the floating catalyst is higher (by approximately 50%) than the coated plate configuration but approximately 50% lower than the titania suspension. It may be mentioned that it was not possible to separate the copper deposited on the titania suspension from the titania particles. In all cases, the slow deposition rate clearly indicates kinetic control, and indeed increasing the agitation did not improve the deposition rate. The superior performance of the suspension is to be expected due to the rotational freedom and high accessibility of the dissolved species to the titania nanoparticles, so that deposition

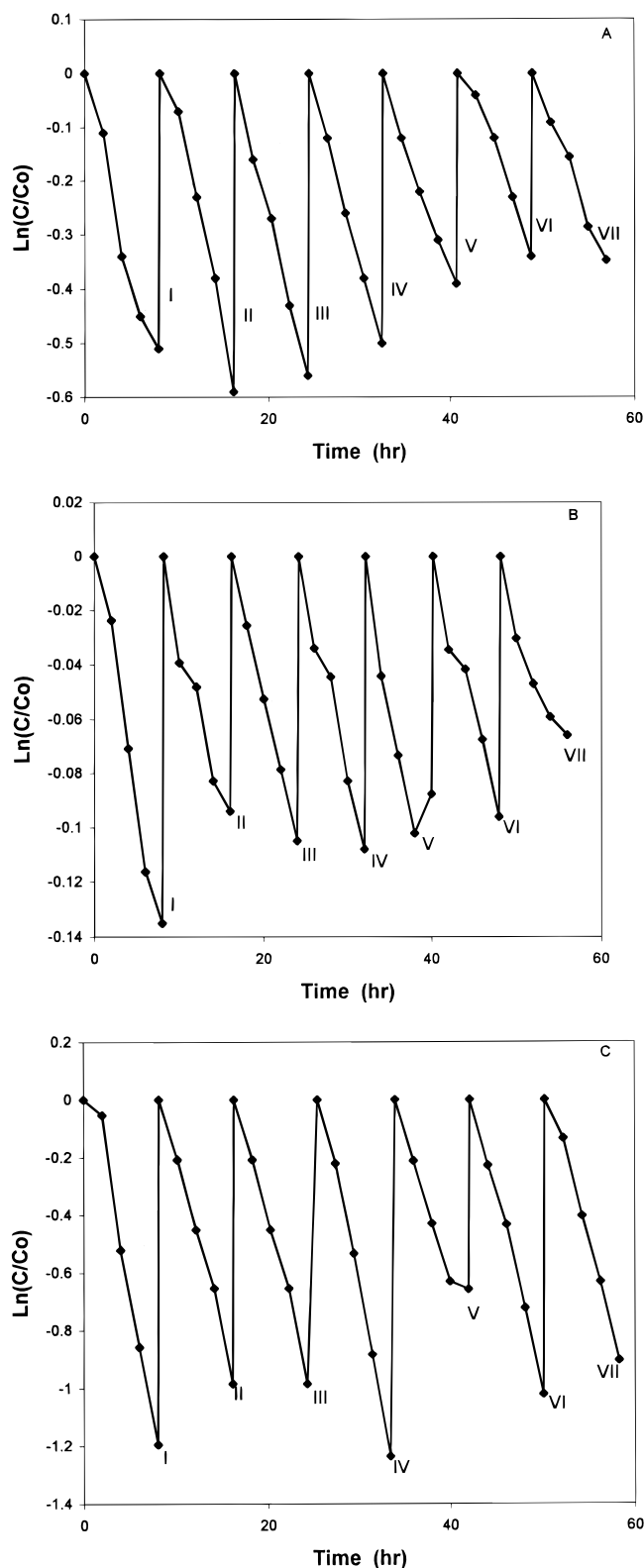


Figure 2. Seven successive kinetic cycles of copper deposition using (A) floating catalyst, 100 mg; (B) titania-coated plate, 6.25 cm²; and (C) titania suspension, 34 mg. The solid lines without the points indicate the readjustment of the CuSO₄·5H₂O concentration to 0.1 M and deaeration with N₂(g) for 30 min. The other conditions are same as in Figure 1B.

and reduction can take place on all sides of the catalyst. The improved performance of the floating catalyst as compared to the titania plate was unexpected since a large fraction of the light is absorbed by the dark graphite and another portion is lost in the unavoidable

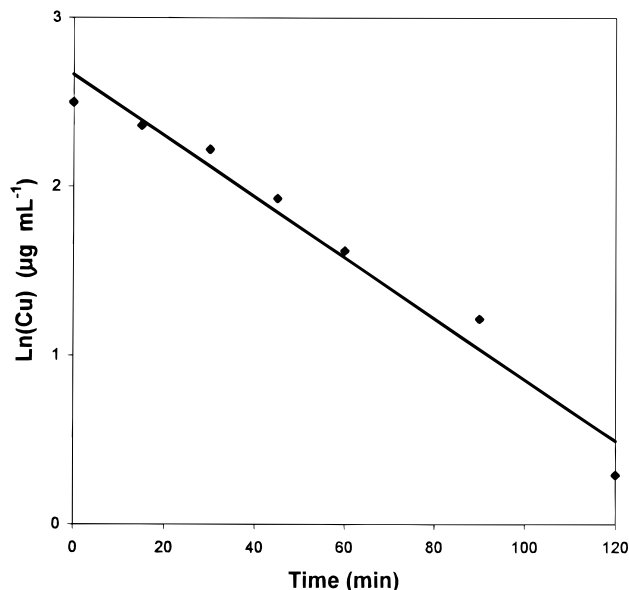


Figure 3. Photodeposition of copper on 100 mg of floating catalyst with initial copper concentration of 0.5 mM, 0.1 M H₂SO₄ and 0.1 M 2-propanol (correlation coefficient $R = 0.98$).

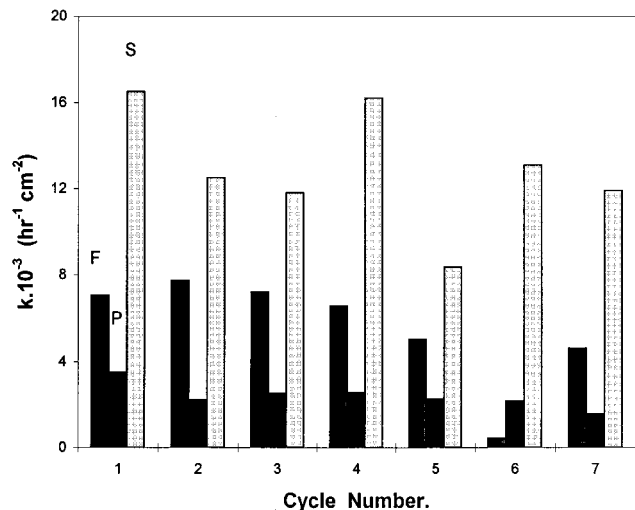


Figure 4. First-order rate constants for floating catalyst (F), plate (P), and suspension (S) for seven cycles of copper deposition with 8 h per cycle.

gaps between the floating pellets. We estimate this gap to be approximately 10–25% of the cross section area. We attribute the increased activity of the floating catalyst, as compared to the flat-plate configuration, to the rotational freedom of the floating particles and to their much rougher surface, which permits unobstructed growth of larger metal crystals (Figure 1B,C). Another possible explanation for the enhanced rate of metal deposition on the composite catalyst stem from the possibility of copper deposition on the conductive graphite, which increases the available surface area for deposition and also minimizes the mass transport shielding of the titania by the metal deposit.

Effect of the Mass of Floating Catalyst and Titania Content on the Rate of Copper Deposition.

The mass of floating catalyst determines the fraction of the available light absorbed by the titania rather than being lost due to absorption by the solution or passed through the cell without being absorbed at all (we assume that reflectance is minimal due to the low reflectance of the graphite support).

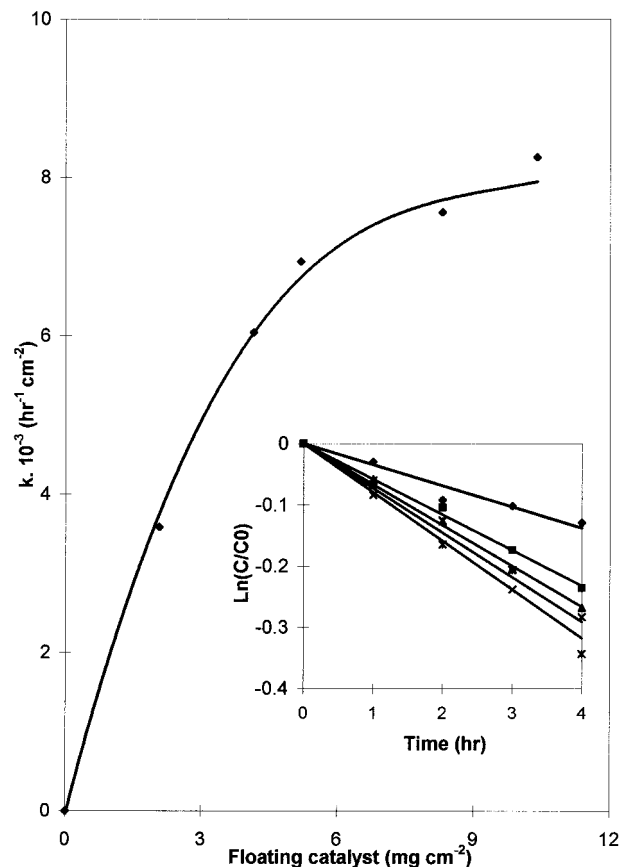


Figure 5. Plot of the first-order rate constant for varying amount of floating catalyst (between 20 and 100 mg; illumination intensity of 225 mW cm⁻²; area of exposure 9.62 cm²). Insert: plot of the natural logarithm of the fraction of Cu(II) remaining in the cell versus time for different mass of the floating catalyst. Curves correspond to 20, 40, 50, 80, and 100 mg of floating catalyst.

Figure 5 demonstrates the dependence of the apparent deposition rate constant on the mass of the floating catalyst used. Almost linear dependence on the mass of the catalyst is observed up to approximately 6.2 mg cm⁻² loading (i.e., 60 mg of catalyst/9.62 cm² cross-section area). At this point the floating catalyst fully covers the cross section area of the cell. An excess amount of the catalyst increases the deposition rate only slightly. This indicates that a second layer of catalyst is shaded by the first layer and is not illuminated by the light source or the reflectance from the first layer. The further small increase in the apparent rate beyond 6.2 mg cm⁻² is an artifact caused by attachment of some of the catalyst to the walls of the cell, thus leaving part of the cross-section area uncovered. When surplus of catalyst is used, this gap is partly filled by the excess catalyst. Therefore, a value of 10.4 mg cm⁻² (100 mg of catalyst/9.62 cm² cross-section area) catalyst was used in studies on the effect of other parameters.

Figure 6 illustrates the effect of varying the percentage of titania in the catalyst on the deposition rate of copper. In all experiments, the ratio between the EG+titania and Ormosil was kept constant, equal to 1, and the same amount of catalyst (100 mg) was used. It can be seen that the plot of the fraction of the Cu²⁺ depleted is nearly linear at low coverage (less than 20%). Surface coverage is determined almost exclusively by the EG and not by the total amount of catalyst. In the presence of excess titania, above 30% (60/200) a decline

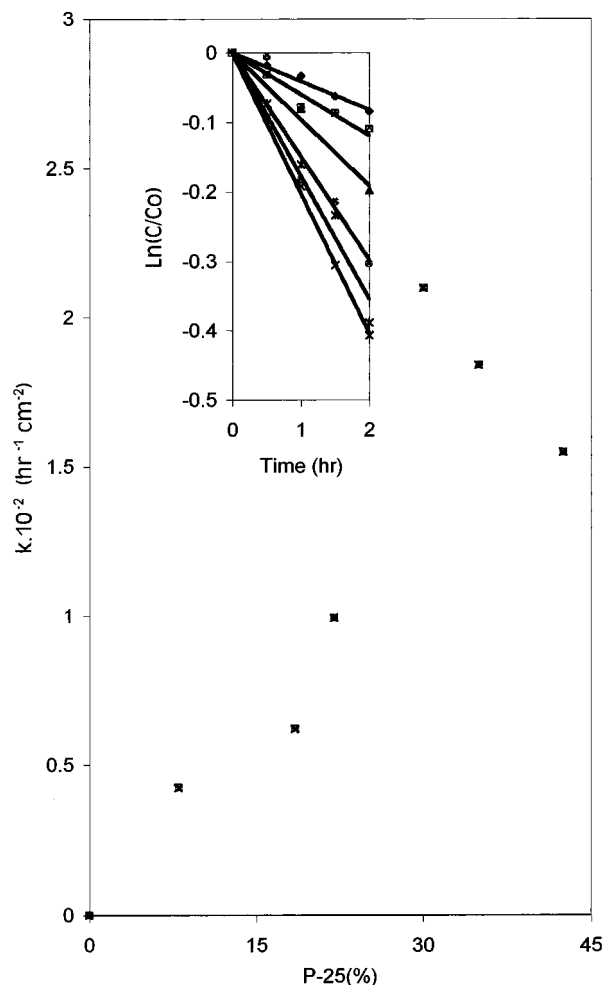


Figure 6. Plot of the first-order rate constant per unit surface area of exposure versus varying titania percent loading in the floating catalyst. Illumination intensity 225 mW cm². Area of exposure 9.62 cm². Insert: plot of the natural logarithm of the fraction of Cu(II) in the cell versus time, for 100 mg of the floating catalyst. Curves correspond to 8, 18.5, 22, 30, 35, and 42.5% titania.

in the rate is observed since full coverage of the floating catalyst by titania aggregates is reached and the lower layers of titania are poorly illuminated and thus less active. Similar dependence was observed in photodegradation studies,¹⁷ though the optimal concentration of titania for copper deposition is slightly lower (30% in the current study versus 33% for photodegradation studies) probably due to the partial coverage of the surface by the bulky metal deposit.

Effect of pH on the Copper Deposition. The change in the first-order rate constant of copper deposition as a function of pH in the range 0.5–4.2 was very mild (for pH values, 0.5, 1.5, 3.6, and 4.2 $\ln(k)$ was -5.5 , -5.6 , -5.2 , and -5.0 1/(h cm) respectively). At higher pH the formation of basic copper sulfates brochantite ($\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$) and antlerite ($\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$) was reported.^{9a} Indeed, the UV/visible spectrum of the solution was independent of the pH in the specified range, and the dark purple color of the basic sulfates was not observed neither on the catalyst nor in the solution, confirming absence of the basic copper sulfates. The photodeposition rate varied by less than 40% in this range. Foster and co-workers^{9a} showed a change of 50% for copper recovery when the pH was increased from 1.8 to 4.5, Foster and co-workers^{9a} reported that at lower

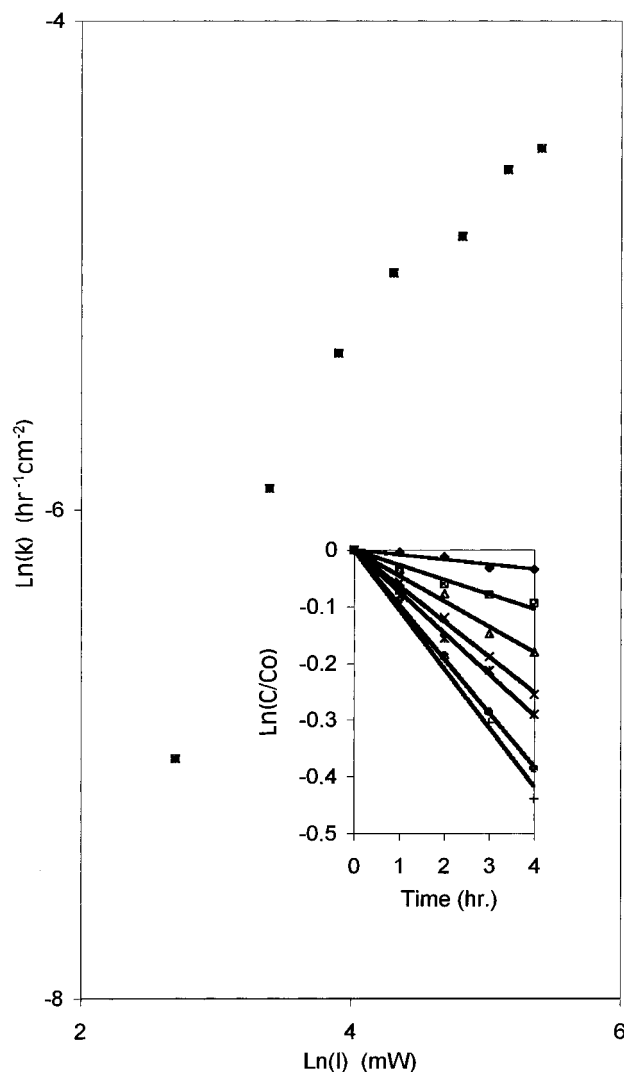


Figure 7. ln–ln plot of light intensity (I) versus the first-order rate constant for 100 mg floating catalyst. Exposed area 9.62 cm². Initial concentration of 0.1 M Cu(II). Insert: plot of the natural logarithm of the fraction of Cu(II) remaining in the cell versus time, at varying light intensities. Curves correspond to 15, 30, 50, 75, 125, 175, and 225 mW/cm².

pH (<1.35) the dominant photoprocess is water splitting. This was not observed in our studies probably because of the higher concentrations of Cu^{2+} used in the current studies. The small increase in rate toward the higher pH range can be attributed to preconcentration of copper ions in the vicinity of the charged surface $\equiv\text{TiO}^-$ groups or to lower repulsion by the $\equiv\text{TiOH}_2^+$ groups (the pzc of titania is ca. pH 6). The very small slope (approximately 0.1 decade/pH decade) is indicative that the dominant mechanism is copper deposition and not the hole-scavenging process, which is pH dependent.

Effect of Light Intensity. Figure 7 illustrates the effect of varying light intensity on the rate of photoreduction of Cu^{2+} on the surface of the floating catalyst. The depletion of Cu^{2+} ions was fitted to first order rate law (Insert, Figure 7) and the rate constant was calculated from the slope of the fitted curves. Figure 7 represents the ln–ln plot of the first order kinetic coefficient of copper deposition and the light intensity. Although the dependence of copper deposition on light intensity is complex (probably due to the heterogeneous nature of the floating catalyst), a linear approximation

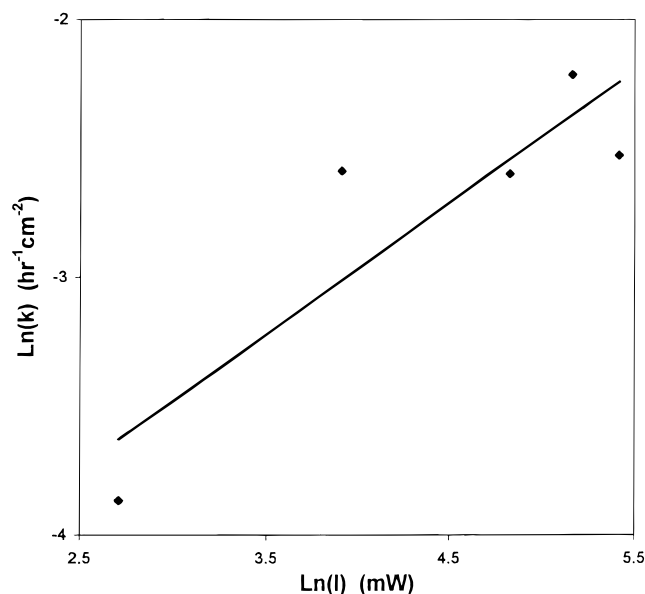


Figure 8. Logarithmic plot of light intensity, versus the first-order rate constant for initial Cu(II) concentration of 0.5 mM (correlation coefficient $R = 0.89$).

($R = 0.96$, RSD in slope = 17%) suggests a first-order dependence on the light intensity at high Cu²⁺ concentrations (0.1 M). Figure 8 shows the dependence of the rate on light intensity at low copper concentrations (starting, 0.5 mM). Here, the ln–ln plot of the rate versus light intensity suggests a half-order dependence ($R = 0.89$, RSD in slope = 10%).

Both linear and square root relationships are frequently encountered for the dependence of the kinetic coefficient on the light intensity. The square root dependence is usually encountered when the rate of electron–hole recombination is high; while when the recombination is negligible, first-order dependence is encountered.¹ This simple mechanistic explanation seems to fit our observations. When the concentration of the copper ions is high, then the rate of the electron utilization is relatively high compared with the electron–hole recombination reaction, thus yielding first-order kinetics. When Cu²⁺ is less available in the vicinity of the crystalline photocatalyst, the surface recombination becomes the dominant mechanism, resulting in lower quantum yields and half-order kinetics.

Effect of Oxygen Concentration. The presence of oxygen was found to be deleterious to the performance of the floating catalyst for recovery of copper in all pH ranges, which practically limits the use of the composite catalyst to oxygen free solutions. The effect of oxygen can be attributed to the competition in electron scavenging and also to the oxidation of copper by traces of oxygen, thus interfering with the ripening of the copper crystals.

Regeneration and Stability. Three types of tests of stability and regeneration capability of the floating catalysts were conducted. In the first, the catalyst was illuminated for over 100 h with a 300 W Xe lamp at 225 mW cm⁻². The catalyst retained full floatability after this period. In a second test we have repeatedly deposited copper, from cupric sulfate solution, replacing the solution with a fresh one after each time the solution was depleted. Each cycle consisted of 8 h after which the spent medium was discarded and the cell was

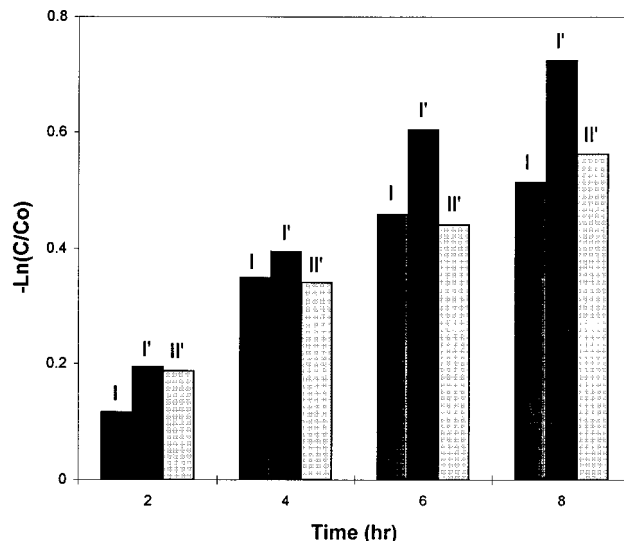


Figure 9. Plot of the natural logarithm of the fraction of Cu(II) remaining in the cell after illumination with fresh catalyst (I) and with regenerated catalysts after one (I') and two (II') cycles of copper deposition and dissolution (100 mg of floating catalyst; illumination intensity, 225 mW cm⁻²; surface area, 9.62 cm²).

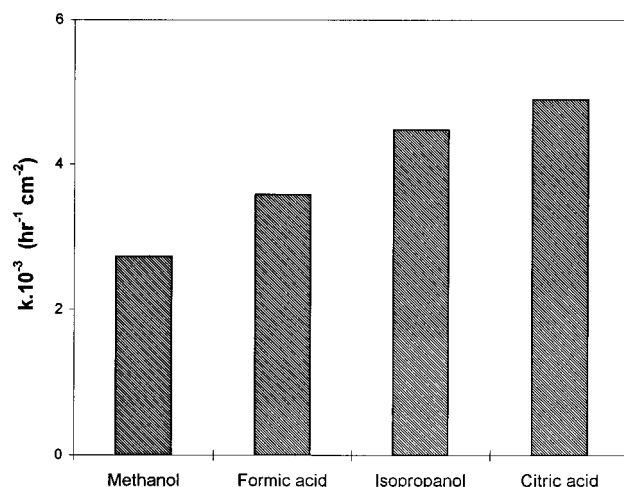


Figure 10. Effect of different organic hole scavengers on the first-order rate constant per unit surface area of illumination for 100 mg of floating catalyst and 0.1 M of methanol, formic acid, 2-propanol and citric acid; 0.1 M CuSO₄·5H₂O in 0.1 M H₂SO₄.

refilled with fresh 0.1 M CuSO₄·5H₂O containing 0.1 M 2-propanol in an acidic medium of 0.1 M H₂SO₄. The floating catalyst loaded in the cell was not changed till the completion of seven cycles (approximately 56 h). The catalyst was stable and maintained its floatation capability even after this period. The catalyst exhibited only small reduction in activity (approximately 30%) during this period (Figure 2A). Similar performance was also found for titania suspension, though the suspension lost floatability almost immediately within the first run. As a consequence, in deeper reactors the suspension would have lost activity while the floating catalyst would still be useful.

To investigate the acid regeneration capability of the floating catalyst, the catalyst was suspended after the seventh cycle in 0.18 N HNO₃ for 24 h, followed by filtration using a Whatmann filter paper (No. 42). The regenerated floating catalyst was dried for 24 h, in a desiccator using CaCl₂ as the desiccant, before reuse.

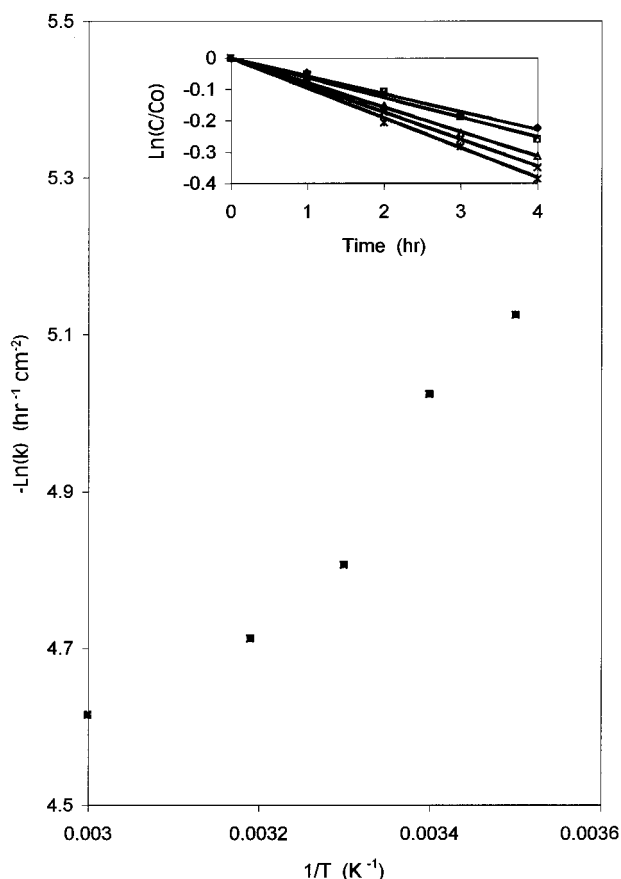


Figure 11. Logarithmic dependence of the first-order rate coefficient on the inverse of the absolute temperature (slope = 1049 K^{-1} , correlation coefficient $R = 0.96$, and RSD in slope = 16%). Insert: effect of temperature on the deposition rate of copper: Curves correspond to 10, 20, 30, 40, and 50 °C. Initial concentration (C_0), 0.1 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 0.1 M 2-propanol; 100 mg of floating catalyst; illumination intensity 225 mW cm^{-2} ; area of exposure 9.62 cm^2 .

Figure 9 demonstrates the ability to reuse the catalyst for Cu^{2+} reduction. Two deposition cycles were carried out, and the first-order rate coefficient for the regenerated catalyst was found to be $1.01 \times 10^{-2} \text{ h}^{-1}$ (I) and $0.81 \times 10^{-2} \text{ h}^{-1}$ (II), comparable to $0.81 \times 10^{-2} \text{ h}^{-1}$ (I) observed for the freshly prepared floating catalyst.

Effect of the Type of Hole Scavenger. The effect of different organic hole scavengers, for the photodeposition of copper, on the surface of floating catalyst is depicted in Figure 10. A plot of the first-order rate constant for reduction of Cu^{2+} using four different organics, methanol, formic acid, 2-propanol, and citric acid, indicates roughly similar k values where $k = 3.93 \times 10^{-3} \text{ h}^{-1} \text{ cm}^{-2} \pm 25\%$. Foster et al.^{9a} demonstrated that a change in the hole scavenger induces more than 2 orders of magnitude change in the deposition rate (at

pH 3.5–3.6) upon changing the hole scavenger from citric acid to methanol. The low dependence of the deposition rate on the hole scavenger used in our studies points to the fact that the electron scavenging by the Cu^{2+} ions and not the hole-scavenging step is the rate-determining step. The low dependence of reaction rate on the type of scavenger as compared to Foster's study is attributed to the low pH used in the current study (pH 1.6), which prevented complexation of copper by the citrate or formate ions (the $\text{p}K_a$ of formic acid is 3.75 and the $\text{p}K_a$'s of citric acid are 3.08, 4.74, 5.4).

Effect of Temperature and Activation Energy.

Figure 11 illustrates the enhancement in copper deposition by the floating catalyst between temperatures of 10–50 °C. A linear approximation of the plot of the inverse of the deposition rate versus of the absolute temperature, (Figure 11) yields an activation energy of $E_a = 20.34 \text{ kJ mol}^{-1}$ ($R = 0.96$, RSD in slope = 16%). This value of E_a is comparable to an earlier report¹¹ of 19.3 kJ mol^{-1} for deposition of platinum on titania suspension. Kamat et al.¹⁹ had attributed the effect of increasing temperature on the photocatalytic rates of titania to the decrease in the bandgap energy of titania with temperature.

Conclusions

On the basis of the above investigations, it could be concluded that the floating catalyst formed between 8 and 42.5% titania in 100 mg of EG using MTMOS as the binder ($r = 7.5$) can be used as a recyclable, regeneratable, and efficient photocatalyst for the removal of copper from an aqueous acidic medium. The property of peeling off, of the copper from the surface of the catalyst, could be used for obtaining pure "Cu metal" for specific applications. The model of metal deposition on such floating catalysts could be extended to other noble metals such as Au, Pt, Pd, and Ag; work is in progress in this direction.

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