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Tech Note: Removal of Heavy Metals by Photocatalyst.

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Abstract.-

In this paper, a removal cations method is analysed by photocatalysis and is studied the influence of different factors for silver removal. This work shows the effect of various parameters on the removal reaction. In that sense, increasing of compound such as alcohol is one of the most important and effective characteristics that could be affect directly on photocatalyst mechanism and this has relation with the properties of photocatalyst, that could produced a hole-electron in chemical reaction, and this is vinculated with a change in the efficiency of reaction.

Keywords: photocatalyst; TiO₂; heavy metal; catalyst.

Nota Técnica: Remoción de metales pesados por medio de fotocatálisis.

Resumen.- En este artículo, se analiza un método de eliminación de cationes mediante fotocatálisis y se estudia la influencia de diferentes factores para la eliminación de plata. Muestra el efecto de varios parámetros en la reacción de eliminación. En ese sentido, el aumento de compuestos como el alcohol es una de las características más importantes y efectivas que podrían verse afectadas directamente en el mecanismo del fotocatalizador y esto tiene relación con las propiedades del este, el cual podría producir un agujero-electrón en la reacción química, y esto está vinculado con un cambio en la eficiencia de la reacción.

Palabras clave: fotocatálisis; TiO₂; metales pesados; catálisis.

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as a photocatalytic oxidation agent and a reductant. [3].

1. Introduction

Metal ions are generally none decomposed. The major source of heavy metals is the improper discharge of various industrial wastewater [1]. Their presence would cause contamination in the environment and also it transfer to human body. The presence of heavy metals in aquatic bodies has been known to causes pollution problems. One of the purpose to use of photocatalyst will be extracting heavy metals from the slurry by mechanical or chemical means. According to definition, photocatalyst is based on accelerate of light reactions in the presence of semiconductor, that is typically TiO₂ [2] and light. Photocatalytic deposition of silver on powder Titania consist in the recovery of silver based in the photocatalytic concept, process in that TiO₂ semiconductor acts

Elimination is very important, especially for valuable metals and recovery of noble metals from industrial waste effluents several water-detoxification photocatalytic devices have already been commercialized. Solar platforms are working with large-scale pilot photoreactors, in which pollutants are degraded with quantum yields comparable to those determined in the laboratory. Catalyst produces an influence in the kinetic and causes accelerating chemical transiting, without changes in the end of the reaction. In addition to heavy metal depollution, this technique is also a promising method for extracting heavy metals from aqueous medium, using TiO₂ powder as photocatalyst. There are other methods for ions removal as: precipitation, activated carbon adsorption, ion exchange, membrane separations, alkaline chlorination or advanced oxidation technologies based on the use of ozone or peroxide, but heterogeneous photocatalysis has shown a higher efficiency[4][5]. It was observed

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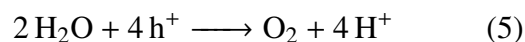
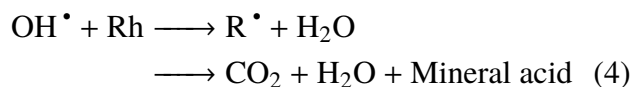
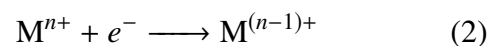
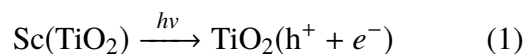
that the photocatalytic reduction occurred on the surface of the catalyst rather than in the bulk solution [6]. Upon irradiation, the consumption of silver ions at the Titania surface would be faster than their diffusion to the surface from the bulk. As a consequence, the rate of silver reduction would be determined by the diffusion process therefore resulting in a decrease of the photoinduced electron transfer reaction at low concentrations of silver ions in the aqueous phase [7]. However with UV irradiation, the excess ions take part in increasing the degradation. This photocatalytic method is based on the reactive properties of electron-hole pairs generated in the semiconductor particles under illumination by light of energy greater than the semiconductor band gap when electron scavenger, such as oxygen, is used to suppress electron/hole recombination, and to allow the photogenerated holes to undergo the anodic reactions, it is called the photocatalytic oxidation. By contrast, photocatalytic reduction takes place when hole scavenger is adopted, and the photogenerated electrons are allowed to undergo cathodic reactions. Two brands of commercially available TiO_2 , Degussa P25 and Hombikat UV100, were chosen as semiconductor photocatalysts for comparative analysis. It is widely known that Degussa P25 TiO_2 catalyst outperforms all other TiO_2 catalysts for photocatalytic degradation of toxic chemicals. Degussa P25 TiO_2 powder is most often used in photocatalytic experiments due to its high efficiency. On the other hand, previous studies have shown the nearly complete removal (99,7%) of dissolved Ag(I) by photocatalytic reduction of AgNO_3 solutions with TiO_2 P25 [8].

UV100 TiO_2 did not exhibit any activity in the photocatalytic reduction of the metal ions studied except for Fe(III) , Hg(II) , Ag(I) , Fe(III) and (VI) could be reduced over P25 TiO_2 [6]. Suitable amount of silver deposited on the surface of TiO_2 could enhance the photocatalytic activity significantly. Silver deposits on TiO_2 surface behaved as sites where electrons and holes on the modified TiO_2 surface allow more efficient of reductions and oxidations. In effect, the semiconductor surface illuminated by ultra violet

light will cause the electron transition from balance band to conduction band, which would obtain the produced electron and hole. In that sense, the electron will be transfer to oxygen molecules or metal ion taking place by reduction due the photogenerated electron, depositing metals on the surface of semiconductor catalyst powder [9]. This article shows the influence of several parameters on the recovery of silver to know the relationship between operational variables or reactants added in the efficiency of reduction, for instance, Szabo-Bardos [3] found that silver photo-reduction on TiO_2 was enhanced in the presence of oxalic acid, at the same time, the authors found a breakdown in the increase of metal deposition rate at various conversions, proposing that the phenomena could be explained by considering the silver ion transport to the surface and its adsorption processes. The present paper analyzes various factors that influence the removal of silver ions from a solution using titanium dioxide TiO_2 in the photocatalysis process and is assumed the removal of metal ions from wastewater.

2. Photocatalysis

The mechanism of photocatalytic reduction of dissolved metal ions is still not very clear but the Redox process is always out lined as follows: Metal ions are reduced by capturing the photo-excited conduction band electrons, and water or other organics are oxidized by the balance band holes. Considering the above, according to the reactions (1), (2), (3), (4) and (5):



The photocatalytic activity with silver deposited was much less enhanced than with platinum, or even detrimental. Nevertheless, silver is most suitable for industrial applications due to its low cost and easy preparation [10]. In presence of organic species Rh, the photogenerated holes in equation (1) are consumed through reactions (3) and (4) to keep the system's neutrality. In the process of photocatalysis, the photogenerated electrons and holes are trapped on the surface and form paramagnetic species [11, 12]. In the absence of other organic species, the conjugate oxidation reaction of metal ion reduction is the electrochemical oxidation of water. This is a kinetically slow four-electron process (equation (5)), and the competing recombination of the photogenerated holes and electrons plays an active inhibiting role [13]. The photogenerated holes have been reported to be trapped at the atoms in the crystal lattice near the particle surface or hydroxyl groups on the surface and should be assigned to trapped electrons rather than trapped holes. The basic fundamental principles are described as well as the influence of the main parameters governing the kinetic (mass of catalyst, wavelength, initial concentration, temperature and radiant flux); any attempt of improving Titania's photoactivity by noble metal deposition or ion-doping was detrimental. If no organic are present, water will be oxidized by reaction (5), and at this point, photocatalytic reduction of metal ions in reaction (2) may be limited by the low rate of water oxidation. [14]. In parallel, heavy toxic metal ions (Hg_2^+ , Ag^+ , noble metals) can be removed from water by photo deposition on Titania surface-trapped photoelectron states, probably Ti(III) , and silver deposition could be observed on the same time scale [15].

3. Efficacy of photocatalyst

The efficacy of photocatalyst depends on factors as follows:

3.1. Effect of potential

Most of the deposited metals that have been previously studies belong to group VIII and

could be reduced using TiO_2 as photocatalyst and considerably increase the photocatalytic activity has been reported in particular with platinum deposited on TiO_2 particle.

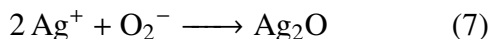
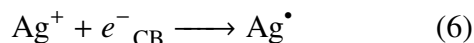
The photocatalytic reduction of a variety of dissolved metal ions in 0,1 wt% TiO_2 (Tioxide Tilcom HACS, 270 m^2/g) suspensions were investigated. They found that only those metals with half-reaction standard reduction potentials more positive than 0,3 V could be reduced using TiO_2 as photocatalyst. Photocatalytic reduction of Ag(I) [23], Au(III) [24], Cr(VI) [25, 26], Hg(II) [27], Pb(II) [28], Mn(II) [29] and Pt(IV) [30] was investigated and reported in the literature. Ag(I) , Au(III) , Hg(II) and Pt(IV) could also be reduced to corresponding metals, and be eliminated efficiently by depositing them onto the photocatalyst Surface. Cr(VI) was reduced to Cr(III) , and subsequently, removed in alkaline medium by precipitation as Cr(OH) . However, no reduction for Cd(II) and Ni(II) [24] was observed according to [1]. The extent of removal of metal ions and potential use under various solution conditions has not been investigated systematically. According to researches, it has shown that the redox potential of the cation metal couple is higher than the flat band potential of the semiconductor. Under identical conditions, the following reactivity pattern was found:

$\text{Ag} > \text{Pd} > \text{Au} > \text{Pt} \gg \text{Rh} \gg \text{Ir} \gg \text{Cu} = \text{Ni} = \text{Fe} = 0$.

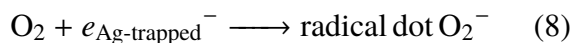
For silver, the deposition initially occurred by forming small crystallites between 3 and 8 nm [16].

3.2. Effect of O_2

The presence of oxygen will be prevented from reduction metal ions, with N_2 purge will be eliminated solution oxygen. Low electron transfer rate to oxygen and high electron-hole pair's recombination rate significantly limit the rate of photooxidant of organic compounds on the catalyst surface [17][18]. The produced holes are important as key elements for pollutant decomposition. This behavior suggested the depletion of Ag^+ ions with the time. The deposition of $\text{Ag}^\bullet$ at the surface of the catalyst and the possible formation of Ag_2O in the presence of O_2 are the two main contributing factors according to equations (6) and (7):



In photocatalytic reduction systems, dissolved oxygen has significant influence on the reduction rate. Dissolved oxygen competes with photogenerated electrons on the surface of the photocatalyst, which is detrimental to the photocatalytic reduction of metal ions. Therefore, it is expected that in the absence of dissolved oxygen, by purging the solution with nitrogen, a higher removal rate of metal ion might be achieved. Dissolved oxygen, acting as electron receptor, significantly inhibited the photocatalytic reduction of metal ions, whose reduction potentials are low [19]. For instance, the photoactivity of silver metal-modified titania particles for sucrose mineralization was observed to decrease by 25% under oxygen-enriched atmosphere in comparison with ambient conditions. Even though oxygen can compete with Ag(I) for scavenging photogenerated electrons, the efficiency of electron transfer from the TiO_2 conduction band to silver ions seems to be more favored than to adsorbed oxygen. The electron transfer from the conduction band of irradiated Titania to the silver particles that are gradually deposited on the semiconductor surface is thermodynamically possible because the Fermi level of titanium dioxide is higher than that of silver. The electronic interaction between deposited metal and semiconductor results in the formation of Schottky barriers at metal-semiconductor contact regions, improving the efficiency of the separation of the photogenerated electron-hole pairs and thus the charge transfers to electron acceptors available on the TiO_2 surface, such as molecular oxygen. Therefore, deposited metallic silver might promote the formation of super oxide radicals through reaction (8):

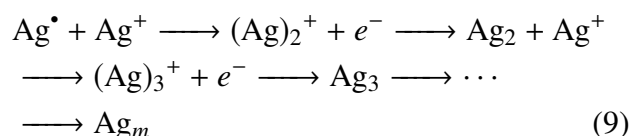


3.3. Effect of light

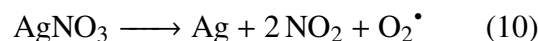
In the presence of light, reaction will be reached to the concentration level of contaminants to

the lowest limited amount in waste water. In addition, the depth of penetration of UV light is limited because of strong absorption by both catalyst particles and dissolved organic species [1] Adequate loading of the semiconductor increases the generation rate of electron-hole pairs for promoting the degradation of pollutants. However, addition of a high dose of the semiconductor decreases light penetration by the photocatalyst suspension [20].

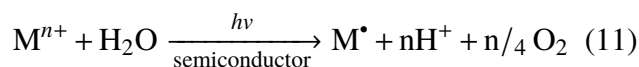
However with UV irradiation, the excess ions take part in increasing the degradation. It was inferred that one-electron, inner sphere reduction of Ag (I) by Ti(III) is rate determining in the formation of the colloidal silver deposit, and that the particles grow by a sequence of alternating Electronic and ionic events, as those proposed in the equation (9).



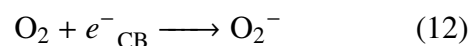
For AgNO_3 and UV system, the concentration of Ag(I) decreased during the UV illumination. The solution when is illuminated turned from white to brown immediately. This is because silver nitrate can easily decompose to silver according to equation (10) once exposed to light, even if the light is not ultraviolet: [21]



Heavy metals are generally toxic and can be removed from industrial waste effluents [8][14] as small crystallites deposited on the photocatalyst according to the redox process in equation (11):



Under oxygenated conditions a high conversion was achieved not only for silver photo deposition but also for cyanide oxidation to cyanate. Therefore, the addition of an electron scavenger (equation (12)) as molecular oxygen might have a beneficial influence on the kinetics of the photocatalytic degradation of dicyanoargentate(I).



3.4. Effect of pH

It was observed that the pH changes measured during the course of reaction provide a deep sight of different processes occurring simultaneously in photocatalytic system. So, pH changes in the solution during irradiation were measured using a pH meter. Ohtani *et al.* [31], indicated similar results with different silver salts. The rate increased with pH (related to a higher adsorption) and varied in the order $\text{ClO}_4^- < \text{NO}_3^- < \text{SO}_4^{2-} < \text{F}^- < \text{PO}_4^{3-}$.

It is worth noting that the positions of both conduction and valence bands are pH dependent. Although, the pH remaining unchanged throughout the Irradiation [19].

4. A typical experiment

Degussa P25 TiO_2 powder is used in photocatalytic experiments due to its high efficiency.

All other chemicals which are used in experiment are shown as follows:

Silver nitrate(99,8%), Methanol (CH_3OH), Propan-2-ol (98%), Sodium cyanide(NaCN), Titanium dioxide (TiO_2), Copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$, 99%), Sodium acetate ($\text{CH}_3\text{COONa} \cdot 3 \text{H}_2\text{O}$) and H_2O_2 (Peroxide Hydrogen). Stock solutions of different materials were prepared by Merk Germany. The irradiation was provided by a 400 W UV lamp. The absorption of the sample was measured by Atomic Absorption SHMADZU 2000, UVICON 922 UV-Visible spectrometer, SVNTEX SP-701 pH-meter measured solution pH.

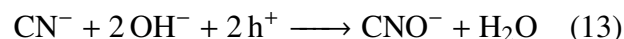
Aqueous AgNO_3 solution containing Cyanide is added with different amount (10, 20, 30, 60 ppm) in certain amount of distilled water, the spent TiO_2 is separated by centrifugation, while the concentration of silver ions in supernatant solution is measured after filtration of the entire irradiated solutions, with atomic absorption spectrometer monitored at 208 nm, in order to identify the products formed during the photocatalytic process. The solution with previously adjusted to pH 7 and TiO_2 catalyst is added to photoreactor, the photoreactor is mounted on a thermo stated reactor holder, under constant stirring. The slurry is magnetically stirred for 30 min in order to achieve

Ag^+ adsorption equilibrium on TiO_2 surface, the absorption spectra of catalysts and silver particles are recorded with UVICON 922 spectrometer. The process uses photogenerated holes at the surface of TiO_2 upon UV irradiation of 400 w. The experiments are conducted at room temperature in air. Also sonication of the spent catalyst followed by sedimentation has been proposed by Barakat *et al.* [6] as a physical method to dislodge large particles of silver from the TiO_2 in case of high Ag loadings [22].

5. Analysis of effects on silver removal by photocatalysis.

5.1. Effect of cyanide concentration

The rate of reduction of silver ions will be remaining without any variation. The co-existence of Ag and CN enhanced the removal efficiency of both Ag and CN. Synthetic wastewater containing both, CN and metal ions was used to investigate simultaneous treatment heavy metals with illuminated TiO_2 . The effect of the presence of cyanide on the removal efficiency of metal ions and adsorption Ag before and after 30 min adsorption was low. No further changes in the adsorbed amount were observed. As a consequence, cyanide ions can be subsequently oxidized by holes, as the detection of cyanate species in the solution proves (equation (13)):

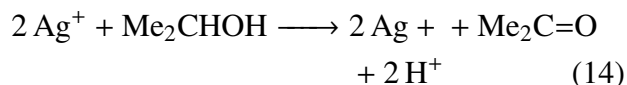


The recombination of photogenerated electrons and holes can be a competing. Such detrimental effect can be partially overcome by the oxidation of the cyanide ions through reaction (13) thus avoiding the recombination of charge carriers [21], a plausible proposal is that the presence of some ions in the solution of chemicals able of stabilizing silver ions in solution as it is the case of CN^- , oxalate or thiosulphate, avoids the complete metal photocatalytic deposition on TiO_2 . This hypothesis is supported by the complete silver removal achieved in the presence of non-complexing sacrificial organics such as 4-nitrophenol. It should be finally mentioned that,

independently of the amount of methanol added, no CN^- mass balance was achieved in any of the reactions.

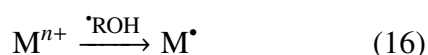
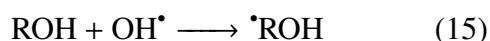
5.2. Effect of 2-propanol

In various irradiation times, have been seen the most rate of silver removal with increasing concentrations of Propane-2-Ol: According the reaction (14) silver ions will be reduced:



Baba *et al.*[32] analyzed the photodeposition of Pt, Ag and Au on an anodically biased TiO_2 electrode in a solution containing alcohols (MeOH, EtOH or 2-PrOH). As no metal deposition was observed.

In the absence of alcohols, they proposed that photogenerated CB TiO_2 electrons do not take part directly in the deposition. Instead of this process, an indirect reduction occurs through the formation of an alcohol cation radical ($-\text{ROH}^\bullet$) produced from the alcohol through attack by OH (equation (15)):



Metal ions as electron capture agents and the action of methanol as a hole-capture agent (equation (16)). Suitable amount of silver deposit on the surface of TiO_2 could enhance the photocatalytic activity significantly. Silver deposits on TiO_2 surface behaved as sites where electrons and holes on the modified TiO_2 surface allow more efficient reductions and oxidations.

The addition of sacrificial electron donors, such as suitable organic substrates, may accelerate the photocatalytic reduction of metal ions. As a consequence, photocatalytic reduction on TiO_2 in metal-organics- TiO_2 must be more efficient than that in metal- TiO_2 system resulting from the accelerating elect by the preferential photocatalytic oxidation of the organics.

In such metal-organics- TiO_2 co-existed system organic.

5.3. Effect of TiO_2 amount

The amount of variation is more in 60 ppm concentration of TiO_2 and consequently, photocatalytic reduction is favored at this concentration.

5.4. Effect of methanol amount

A Linear dependence is observed at low concentration of CH_3OH and any dependence at higher concentrations. On the basis of the above considerations, the influence on the kinetics of the addition of sacrificial electron donors was investigated by performing further experiments in the presence of methanol. As it is well known, this alcohol behaves as an efficient scavenger of holes in photocatalytic reactions thereby suppressing the electron-hole recombination. The process by which methanol acts as an efficient hole scavenger in photocatalytic reactions has been described in the literature as follows. The reaction of photogenerated holes with hydroxyl groups leads to formation of OH radicals (reaction (3)) that readily react with methanol molecules through abstraction of a hydrogen atom from the C-H bond therefore generating α -hydroxymethyl radicals (reaction (17)).



The α -hydroxymethyl radicals formed are species with a strong reducing power that can either inject an electron into the conduction band of the semiconductor, process known as current doubling effect or react with other species adsorbed on the Titania surface. Data available in the literature on the redox potential of α -hydroxymethyl radicals indicate they have enough reducing power for converting Ag(I) from $\text{Ag}(\text{CN})_2^-$ in Ag^0 .

In the presence of oxygen, however, the improvement of Ag(I) reduction induced by methanol is significantly diminished. It is suggested that in this case, α -hydroxymethyl radicals preferentially react with O_2 , thus fading their reductive role. Formation of formaldehyde as the dominant stable product in a quantitative reaction between $\text{CH}_2\text{OH}^\bullet$ radicals and molecular oxygen ($k = 9,6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) has been

previously reported. Summarizing, the role of methanol as hole scavenger thereby decreasing carriers recombinations would not be affected by the reaction environment. On the contrary, the availability of $\cdot\text{CH}_2\text{OH}$ reducing radicals to enhance the reduction of Ag(I) from the complex to metallic silver would be limited to anoxic conditions, as in aerobic conditions the predominant reaction is the photocatalytic oxidation of the alcohol with O_2 participation.

6. Conclusion

Environment pollution is one of the most important problems that human beings are dealing with. Metal cation is one of them which have been entered by wastewater of industrial factories at environment and it is one of the environmental pollutant, they are such as Pb, Ag, and Cu. In that sense photocatalysis process was analysed founding that increasing of compound such as cyanide, alcohol, acetate is one of the most important and effective characteristics that could be affect directly on the photocatalyst mechanism. This is based on the compound properties of photocatalyst that could be reacted hole-electron in chemical reaction and with improving them we can change their efficiency reaction. Effect of propan-2-ol is more notory than methanol on the rate of reduction of silver ions and it could to produce of stability carbonation than methanol.

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