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Removal of Cadmium (Ii) Using A New Photo Catalyst $SrWO_4$ – A Photo Catalytic Remedy for Purification of Water

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Abstract: *The Contamination of water by toxic heavy metals is a world-wide environmental problem. Cadmium, in particular, is found toxic and of enormous harm because of its tendency to accumulate in the tissues of living organisms. The goal of this research is to treat low concentration cadmium bearing water using photo catalysis technique. Present work incorporates the removal of Cd(II) using $SrWO_4$ as a semiconductor. The progress of reaction is observed spectrophotometrically. The effect of variation of different parameters like pH, concentration of Cd(II), amount of photocatalyst, light intensity etc. on the rate of reaction was observed. A tentative mechanism for the reaction is proposed.*

Keywords: *Reduction, pseudo first order kinetics, pH, light intensity, semiconductor, concentration of Cd(II) etc.*

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I. Introduction

Photo catalysis science 1938 has been found to be a promising water treatment method. In recent years, array of industrial activities have been disturbing the geological equilibrium of metal ions through release of large quantities of toxic metal ions into the environment. As a result, in today's industrialized society we are living in an environment with a multitude of potentially harmful toxic metal ions. Thus as time passed, a need to remove these metal ion drew attention of scientists. Discharges containing Cadmium, in particular, are strictly controlled due to the highly toxic nature of this element and its tendency to accumulate in the tissues of living organisms. Cadmium is introduced into bodies of water from ferrous and nonferrous smelting, metal plating, cadmium-nickel batteries, phosphate fertilizer, mining, pigments, stabilizers, alloy industries and sewage sludge.

Removal of trace amount of metal ions from waste water using Alizarin Red S bounded on polyurethane foam was suggested by Moawed[1]. Photocatalytic reduction of chromium in aqueous solution by Fe^{3+} doped TiO_2 nanoparticles was carried out by Thakare and Jugele[2] while the photocatalytic reduction and recovery of copper by polyoxometalates was examined by Papaconstantinou et al.[3] Wang and Wan studied[4] the photo electrochemical reduction of cupric ions over TiO_2 was extensively. Photocatalysis for the treatment of water contaminated with metals and organic chemicals in TiO_2 suspension was also reported by Marlinez.[5]

Effects of Bismuth Vandate and Anthraquinone dye on the photo degradation of polycarbonate was a step forward towards use of binary oxides as photocatalyst[6]. The photocatalytic degradation of nickel from waste water using iron (III) oxide [7] and using ultraviolet -irradiated TiO_2 [8]was also investigated. Photo catalytic reduction of pollutant Hg(II) ion was studied on the surface of doped WO_3 dispersion[9] and on two commercial TiO_2[10] while removal of divalent heavy metal ions from aqueous solutions by Dowex HCR-S synthetic resin was reported by Bayar et al.[11] Appleton studied[12] application of a carbon sorbent for the removal of cadmium and other heavy metal ions from aqueous solution. Photo reduction of Cr(VI) ions in aqueous solutions by UV/TiO_2 photo catalytic processes was carried out by Hsiang et al.[13] Nanomaterials as sorbents to remove heavy metal ions in wastewater treatment was investigated by Fu and Wang[17]. Removal of heavy metal ions was carried out by using alumina [18] and alumina coated carbon nanotubes[19]. Wooden materials was also used for the removal of heavy metal ions from water[20]. Removal of heavy metal ions from water by magnetic cellulose-based beads with embedded chemically modified magnetite nanoparticles and activated carbon was studied by Yu et al.[21] Removal of heavy metal ions using a functionalized single-walled carbon nanotube was investigated by Singh et al.[22]

The harmful effects of cadmium include a number of acute and chronic disorders, such as "itai-itai" disease, renal damage, emphysema, hypertension, and testicular atrophy. The drinking water guideline value recommended by World Health Organization (WHO) is 0.005mg Cd L^{-1}. Activated carbon adsorption, precipitation, ion exchange and membrane separations are common methods currently adopted for the disposal or recovery of metal ions in waste water. Reduction by semiconductor photo catalysis is a relatively new technology for the removal of metal ions at ppm level. Therefore the present study was undertaken which deals with the photo catalytic reduction of Cd (II) in aqueous solution over $SrWO_4$ powder.

II. Methods And Materials

Semiconducting powder $SrWO_4$ was prepared through a precipitation reaction between $SrCl_2$ and Na_2WO_4 [14]. The precipitate was washed with distilled water a number of times and dried. Stock solution of cadmium nitrate was prepared in doubly distilled water. The photo catalytic reduction of cadmium nitrate was observed by taking 100mL solution (3.60 ppm) in a 150mL beaker and 0.40g of strontium tungstate was added to it. Irradiation was carried out by keeping whole assembly exposed to 1000W halogen lamp (Okano, Light intensity 54.0m W c m^{-2}). The intensity of light was measured with the help of a solarimeter (Surya Mapi Model CEL 201). A water filter was used to cut out thermal radiation. The pH of the solution was measured with a digital pH meter (Systronics Model 324). The desired pH of the solution was adjusted by the addition of prestandardized HCl and NaOH solution. The progress of the photo catalytic reaction was observed by taking absorbance at regular time intervals using Atomic Absorption Spectrophotometer (Varian AA240 FS Model).

III. Result And Discussion

The photocatalytic reduction of $Cd(NO_3)_2$ was observed by AAS at wavelength 228.8 nm. The results of a typical run are given in table1 and represented graphically in figure 1. It has been observed that plot of log concentration versus time is linear, which indicates that this photocatalytic reduction follows pseudo first order kinetics. The rate constant is calculated by

$$\mathbf{K = 2.303 \times slope}$$

It is observed that there is no change in concentration in absence of semiconductor. This clearly suggested the effect of light on reduction and so photo catalytic reaction was carried out in present investigations.

Effect of pH

The effect of pH on the rate of reduction of Cd(II) was studied in the pH range 2.0-6.5 .The result is shown in figure-2.

It was observed that with the increase in pH, rate of reduction increases. After attaining maximum value (pH 4.0), rate decreases. It is established that surface properties of semiconductor are responsible for photocatalytic process. The hole generated by semiconductor creates H^+ ions in the solution from water .These protons are utilized by dissolved oxygen in solution.

$$2h^+ + H_2O \longrightarrow 1/_2O_2 + 2H^+ \quad \text{...........} \quad \text{(i)}$$

$$2H^+ + O_2(\text{In Solution}) + 2\bar{e} \longrightarrow H_2O_2 \quad \text{.................(ii)}$$

These two reactions counter balance each other to a particular extent. The surface charge on the semiconductor-electrolyte interface will play a major role in deciding the fate of this photo catalytic reduction[15]. The surface charge on semiconductor is responsible for transfer of electrons to Cd(II) converting it into Cd metal**.** The surface charge on semiconductor favors the reduction when it is positive. This surface charge depends on the pH of the solution being positive in acidic medium and negative in alkaline medium. After a particular pH net charge on semiconductor surface becomes zero and is called point of zero discharge (PZC) [16]. When the pH of the solution is low, reaction (i) dominants and reduction of Cd(II) takes place. As the pH is raised reaction (ii) starts dominating the reaction (i), so that there is an additional decrease in the amount of H^+ ions and hence the decrease in rate of photo catalytic degradation of Cd(II) is observed. The reduction of Cd(II) to its lower oxidation state will also adversely affect the value of PZC and this reduces the rate of reaction.

Effect of Cadmium (II) Concentration

In the present study the concentration of cadmium nitrate varies between range 1.85-10.00 ppm. The effect of change in concentration of Cd(II) on the rate of reaction was observed, with keeping all other factor identical. The results are reported in figure-3. It was observed that as the concentration of cadmium nitrate increases, the rate of reaction increases. After a maximum value (3.60 ppm), decrease in the rate of reaction was observed with further increase in concentration. This may be explained on the ground that at larger concentrations, the movement of cadmium ions towards semiconductor surface will be hindered, which will not permit cadmium ions to reach the desired site within the limited time domain and hence, a decrease in the rate of photo catalytic reaction was observed.

Effect of Amount of $SrWO_4$

The effect of amount of photocatalyst on the rate of photo catalytic reduction of Cd(II) was observed by taking different amounts of semiconductor, keeping all other factors constant. The results are reported in figure-4.

As evident from the data, the rate of photocatalytic reduction of Cd (II) increases with increasing the amount of photocatalyst. After a certain amount of semiconductor (0.40g), the rate of photo catalytic degradation becomes constant. Any further increase in amount of semiconductor shows no increase in the rate of reaction.

It can be explained on the basis that as the amount of semiconductor is increased, more particle are available for excitation and there is greater possibility of electron–hole pair generation on exposure to light. This results into a corresponding increase in the rate of reaction. After a certain amount (0.40g), the bottom of the reaction vessel is almost covered and now any addition of semiconductor does not increase the exposed area, rather it only adds to the thickness of the layer of semiconductor at the bottom of the reaction vessel. It was confirmed by the fact that as vessel size is changed, value of k changes and as solution is stirred, rate increases due to increase in number of particle exposed to light.

Effect of Intensity of light

The intensity of light reaching the semiconductor surface is varied by placing reaction vessel at different places beneath the lamp. The results are reported in figure-5. It has been observed that the rate of photocatalytic reaction increases with increasing the light intensity. It is attributed to the fact that more electron-hole pairs will be generated due to an increased number of photons striking the semiconductor surface with increase in the intensity of light. Therefore more electrons will be available for reduction, resulting into the increase in rate of reaction.

IV. Mechanism

On the basis of the observed experimental data, the following tentative mechanism has been proposed for the photo catalytic reduction of Cd(II).

$$SC \xrightarrow{h\nu} \bar{e}\ (CB) + h^+\ (VB) \quad \text{..................} \ (iii)$$

$$2h^+ + H_2O \longrightarrow 1/_2O_2 + 2H^+ \quad \text{..................} \ (iv)$$

$$2H^+ + O_2(\text{In Solution}) + 2\bar{e} \longrightarrow H_2O_2 \quad \text{......................} \ (v)$$

$$Cd\ (II) + 2\bar{e} \longrightarrow Cd \quad \text{..................} \ (vi)$$

In the first step, the semiconductor is excited by the absorption of light of an appropriate wavelength. An electron from the valance band of the semiconductor jumps into its conduction band, leaving behind a hole. This hole is utilized by the water molecule to generate oxygen and H^+ ions. These H^+ ions and dissolved oxygen in solution are reduced by two electrons to form hydrogen peroxide, which slowly degrades. In the last step Cd(II) accept two electrons from conduction band of the semiconductor and reduces to its metallic state. In acidic medium reaction (iv) dominates and thus production of more electrons reduces more Cd(II) substrate increasing the k value. As the pH is raised, reaction (v) starts dominating resulting into decrease in rate of reduction.

The photocatalytic reduction process is an efficient route for the removal or the recovery of cadmium and other metals. The process involves absorption of light by $SrWO_4$ results into reduction of Cd(II) to its metallic state in a two electron process. This method is applicable at ppm level of metal contaminants which not only makes the industrial effluents less toxic, but, it provides an effective way to recover such metals.

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Table –1

pH = 4.0, **[Cadmium nitrate] = 3.60ppm,**
Temperature = 302K, **$SrWO_4$= 0.40g**
Intensity of light = 54.0 mW cm^{-2}

Time (in min.)	Concentration(C) (ppm)	1+LogC
0	3.60	1.5563
30	3.00	1.4713
60	2.50	1.3979
90	2.04	1.3096
120	1.76	1.2455
150	1.46	1.1644
180	1.20	1.0792
210	0.96	0.9823
240	0.82	0.9138
270	0.72	0.8573
300	0.64	0.8573

K= 0.987x10^{-6} sec^{-1}

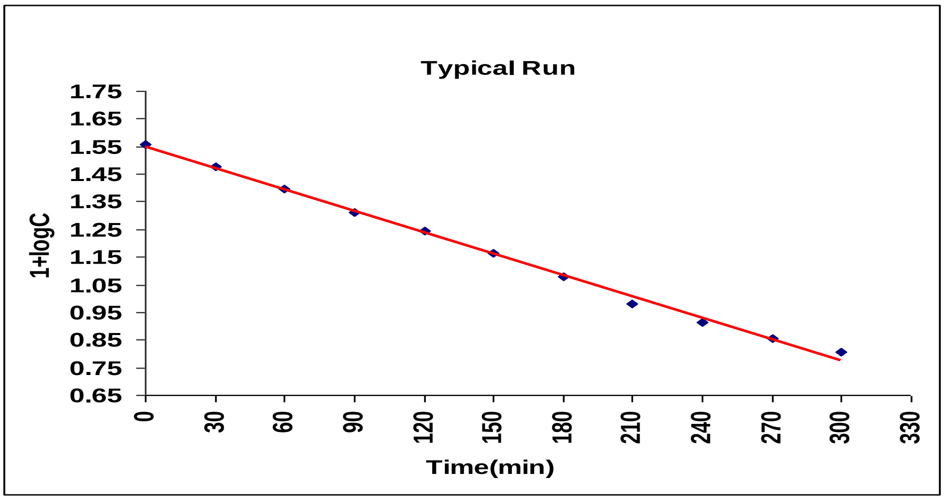

Figure 1: Graph between 1+logC and Time

Effect of pH

[Cadmium nitrate] =3.60ppm, Temperature = 303K, $SrWO_4$= 0.40g, Intensity of light = 54.0 mW cm^{-2}

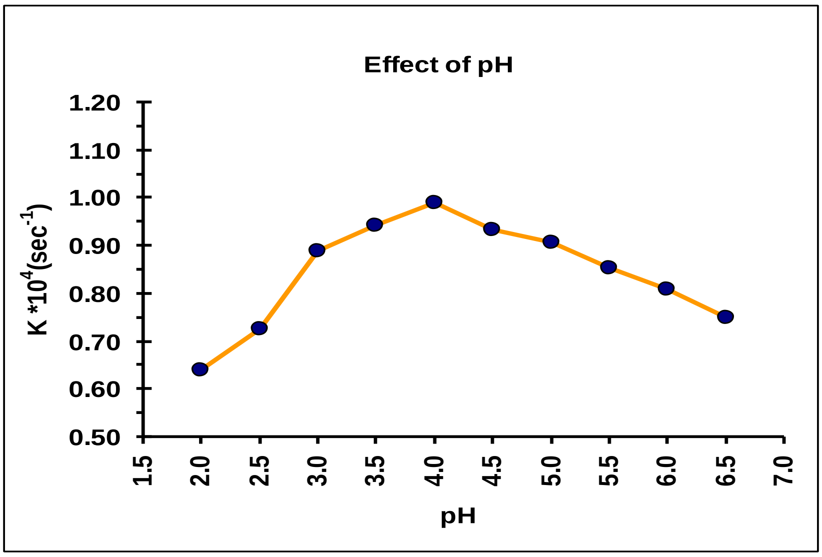

Figure 2: Graph between K and pH

Effect of cadmium nitrate concentration

pH = 4.0, Temperature = 303K, $SrWO_4$= 0.40g, Intensity of light = 54.0 mW cm^{-2}

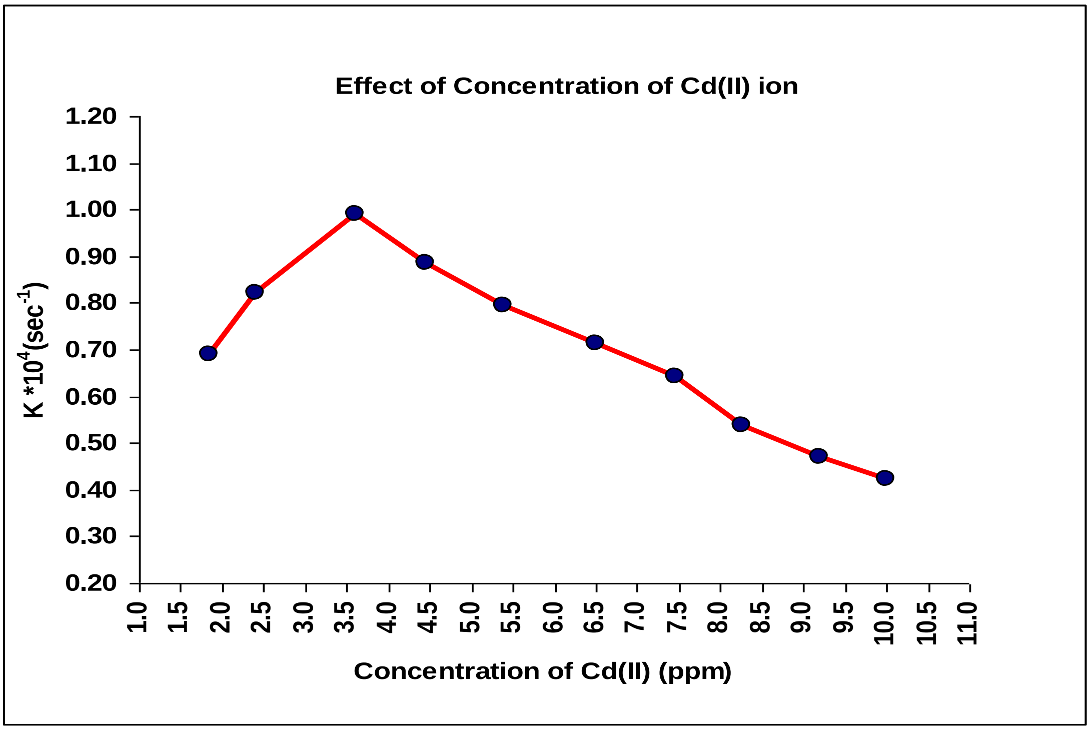

Figure 3: Graph between K and concentration of Cd(II) ppm

Effect of amount of photocatalyst

[Cadmium nitrate] = 3.60ppm, Temperature = 303K, pH = 4.0, Intensity of light = 54.0 mW cm^{-2}

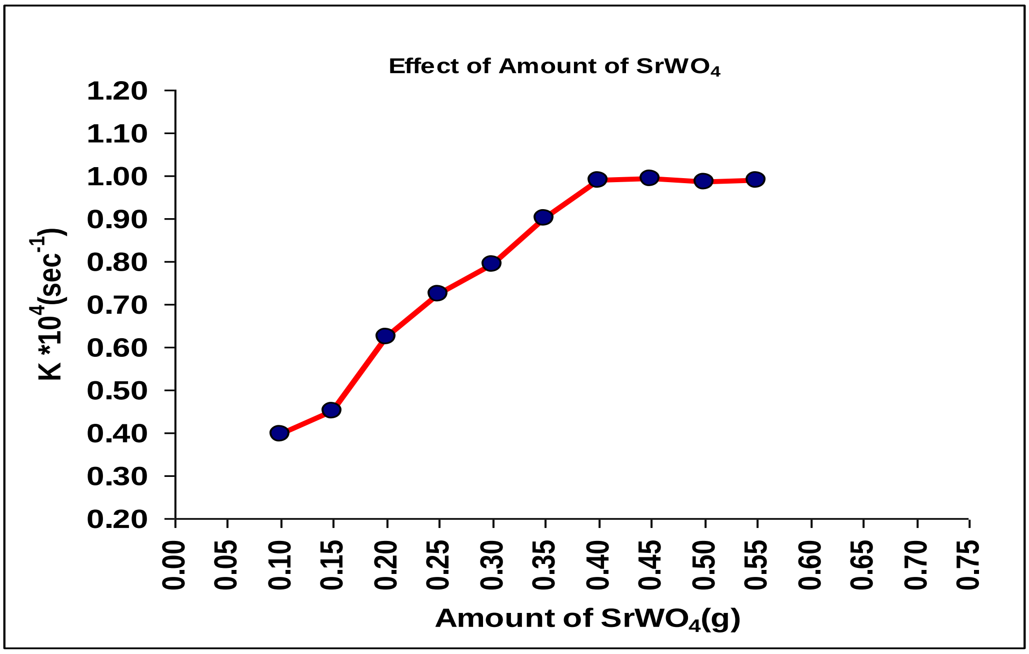

Figure 4: **Graph between K and amount of $SrWO_4$**

Effect of Light Intensity

[Cadmium nitrate] = 3.60 ppm, Temperature =303K, pH = 4.0, $SrWO_4$ = 0.40g

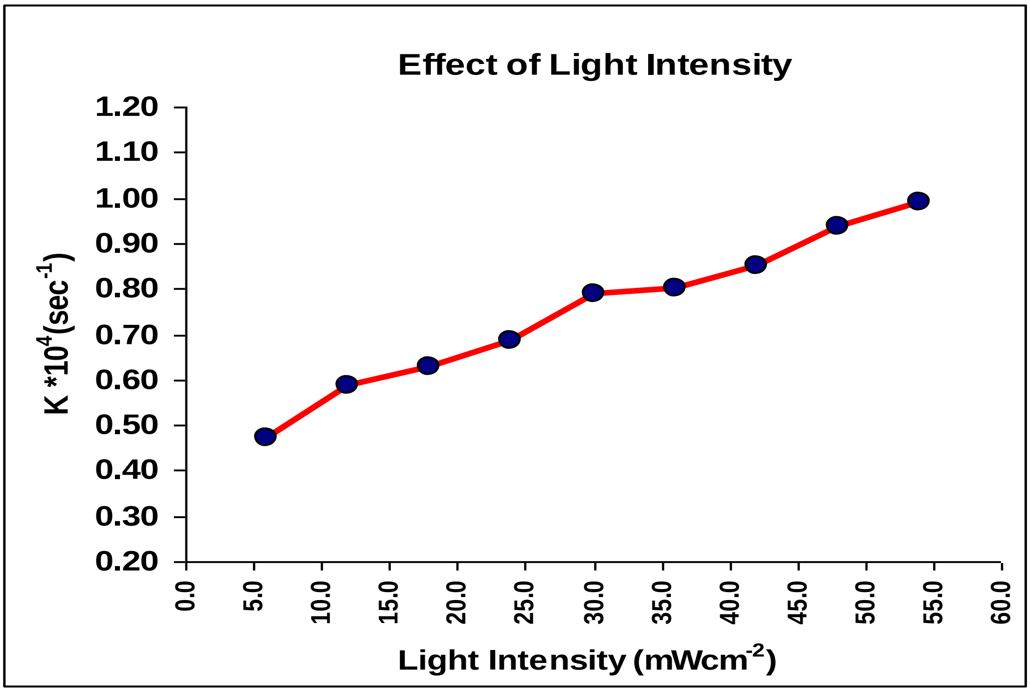

Figure 5: **Graph between K and intensity of light**

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