Degradation of Brilliant Green by Using a bentonite Clay-Based Fe Nano Composite Film as a Heterogeneous Photo-Fenton Catalyst.

Khulood Abid Saleh AL-Saade * **Shatha Fadel Al- Saidi****
Hamdia Hateem Juad***

*Department of Chemistry, College of Science, University of Baghdad.
**Department of Chemistry, College of Science, University of Nahrain.
*** Department of Chemistry, College of Science for Women, University of Baghdad

E-mail: Khuloodabid@yahoo.com

Abstract:

This paper aims to study the chemical degradation of Brilliant Green in water via photo-Fenton (H_2O_2/Fe^{2+}/UV) and Fenton (H_2O_2/Fe^{2+}) reaction. Fe- B nano particles are applied as incrustation in the inner wall surface of reactor. The data form X- Ray diffraction (XRD) analysis that Fe- B nanocomposite catalyst consist mainly of SiO_2 (quartz) and Fe_2O_3 (hematite) crystallites. B.G dye degradation is estimated to discover the catalytic action of Fe- B synthesized surface in the presence of UVC light and hydrogen peroxide. B.G dye solution with 10 ppm primary concentration is reduced by 99.9% under the later parameter 2ml H_2O_2, pH= 7, temperature =25°C within 10 min. It is clear that pH of the solution affects the photo- catalytic degradation of B.G dye. All the conditions above have been studied to reach the optimum operation condition for the two processes Fenton and photo- Fenton. The B.G degradation process follows first- order reaction rules. Photo- Fenton process causes a more efficient oxidation rate than the Fenton process. So, the photo- Fenton degradation is an effective and economic process by producing higher percentage of degradation and mineralization in short radiation time.

Key words: Advanced Oxidation Processes, Fenton, Photo-Fenton, B.G dye.

Introduction:

All dyes molecules are stable and difficult to degrade biologically [1], so they lead to pollution problems like a form of colored waste water discharged; into environmental water bodies [2]. The adsorption procedure is the most efficient method for removing the pollutant dyes form waste water [3-5]. The dye will be transferred to solid phase thereby keeping the effluent volume to a minimum [6-8]. Also the adsorbent can be used more than one time by being regenerated and stored in a dry place [4-8]. The brilliant green dye as used in this study is triphenyl nitrogen containing cationic dye. The

exact structure of the brilliant green dye is given in Figure (1). Brilliant green is chemically described as ammonium, 4(diethylamino)-alpha-phenylbenzylidene) ($C_{27}H_{34}N_2O_4S$) with λ_{max}=625 nm and molecular weight 482 g. mol^{-1}. The use of brilliant green (B.G) dye has been banned in many countries due to its carcinogenic nature [1].It is used as a dye to color synthetic fibers and silk biological stain, dermatological agent, veterinary medicine, and as an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus.It is also extensively used in textile dying and paper printing. It is considered highly toxic for humans and animals because it can cause permanent injury to eyes. It also causes irritation to the respiratory tract that leads to cough and shortness of breath. It can cause irritation to the gastrointestinal tract, which also results in nausea, vomiting and diarrhea in human beings [9].
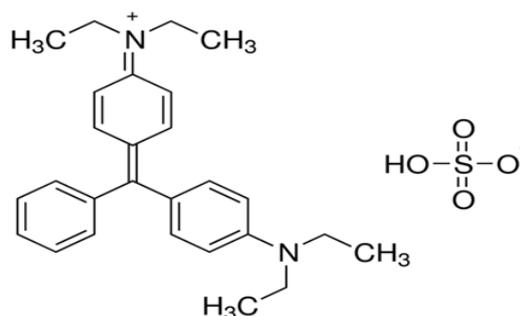
Fig. (1): Structure of Brilliant Green

(AOP's) have been developed during the past ten years and various kinds of advanced oxidation processes (AOP's) are used to remove organic pollutants from waste water. Principled (AOP's) are based on the generation of OH radicals in the solution. These OH radicals then will be responsible for the oxidation of organic compounds and act with non-selectivity. The photo reaction will cause the formation of OH radicals and regeneration of Fe^{2+} which can be expressed as follows [10]:

$$Fe^{2+} + H_2O_2 \xrightarrow{\ \ UV\ \ } Fe^{3+} + \overset{\cdot}{O}H + OH^-$$

$$Fe(OH)^{2+} \xrightarrow{\ \ UV\ \ } Fe^{2+} + \overset{\cdot}{O}H$$

Materials and Methods:

1. Materials:

Birilliant green (B.G) as used in this study is obtained from Merck com. On the other hand, H_2O_2 (30%), Fe$(NO_3)_2.9H_2O$, H_2SO_4, NaOH, Na_2CO_3 and HCl (37%) are obtained from Sigma com. All predation is achieved using double distilled water. The bentonite clay used in present study is supplied from Geological Survey in Ministry of Industrial mineral, Baghdad, Iraq.

2. Preparation of Catalyst:

The preparation of Fe- bentonite nanocomposite flows in the following steps: an aqueous dispersion of bentonite clay is prepared by adding 10g bentonite clay to 500 mL H_2O under vigorous stirring for 3 hs at 25°C. Sodium carbonate is added slowly as a powder into a vigorously stirred 0.2 M

solution of iron nitrate for 3h such that a molar ratio of 1:1 for [Na^+]/ [Fe^{3+}] is established. 500 mL solution from the second step is added drop by drop into the dispersion of bentonite clay prepared in the first step under vigorous stirring. The suspension is stirred for 3hs followed by ageing at 100°C in an autoclave for 48h and finally 1000 mL solution containing Fe-B nanocomposite is obtained for the coating of the Fe-B nanocomposite on the stainless steel plate substrate. The coating of Fe-B nanocomposite on the inner wall surface of photo- reactor is conducted by thermal spray method [11]. The photo-reactor is made of stainless steel pipe with diameter of 4 cm and length 15cm, as shown in Figure (2).
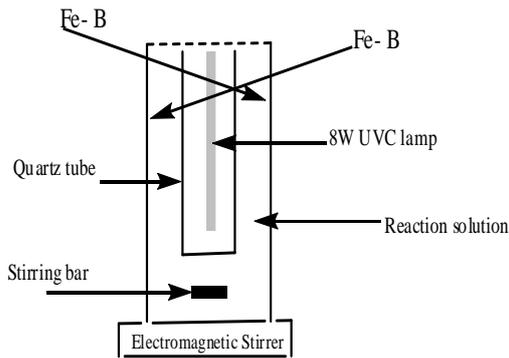
Fig. (2): Experimental Set- up of the Photo- Reactor Coated with A Fe- B [12].

3. Preparation of Dye Sample:

Standard stock solutions of 500 mg/L of brilliant green are prepared by diluting the corresponding mass of brilliant green in de- ionized water and protected from light. A different initial concentration of brilliant green is prepared by further diluting the standard stock solutions.

Results and Discussion:
1.   Characterization of the Catalyst:
1.1   XRD:

(SHIMADZU 6000 X-Ray) X- ray diffraction is used to analyze Fe- B nanocomposite, and the result is shown in Figure (3). The strong diffraction peaks at 2Θ of ($25.5°$, $26.2°$) indicate that the Fe-B nanocomposite mainly consists of SiO_2 (quartz) and ($33.15°$, $39.28°$) Fe_2O_3 (hematite).The increasing in particle size lead, to higher intensity of diffraction pattern[13].
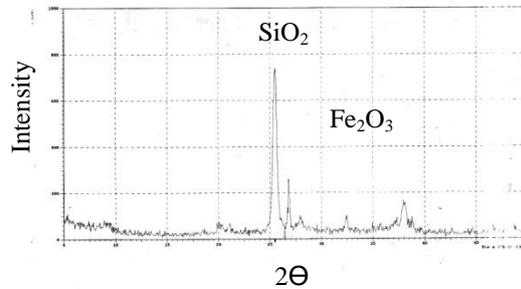
Fig. (3): XRD for: Fe-B nanocomposite

1.2 AFM Analysis:

Atomic force microscope (AFM, AA3000 of Angstrom Advanced Inc. USA), is used to investigate Fe- B nanoparticles.

AFM analysis represents data in three dimensions, so that it is possible to measure the height of the nanoparticles quantitatively. Figure (4) explain the particle size is less than 100nm and show the morphology of nanoparticle and the average particle size of   Fe-B nanocomposite is around 80 nm.
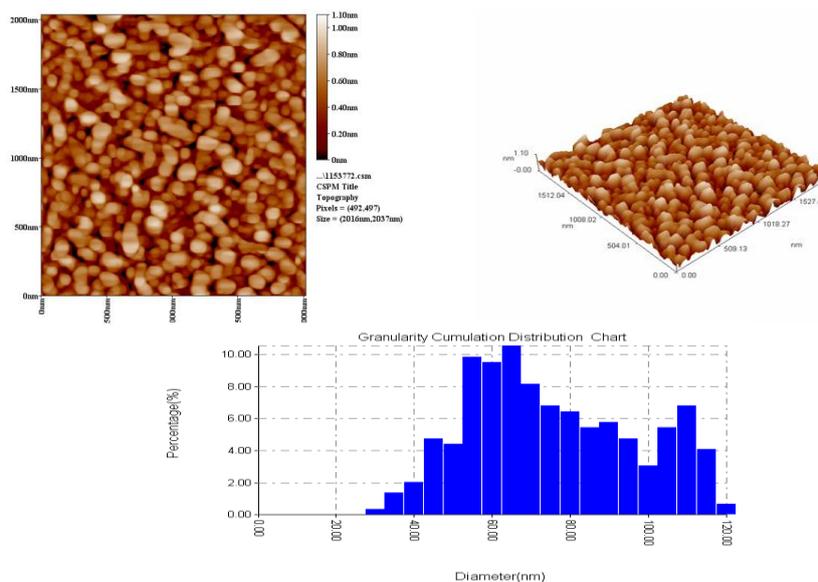
Fig. (4): AFM of Fe- Bentonit Nano composite

2- Degradation of Brilliant Green:

Figure (5) shows the calibration curve for B.G which is determined in λ_{max}= 624 nm that obeys the (Lambert beer's law) at specific concentrations prepared for each compound. After that, the absorption has been recorded and a calibration curve is plotted between adsorption and concentration, the best line between the points has been drawn.
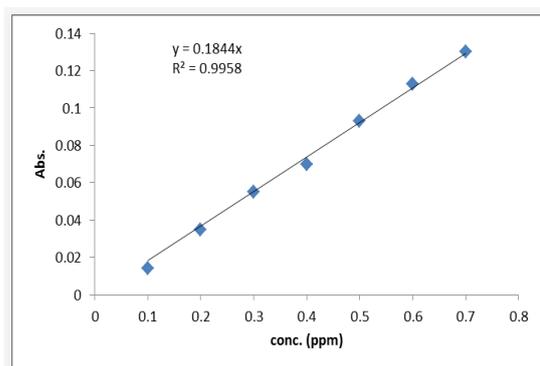
Fig. (5): Calibration Curve of B.G at λ_{max}= 624 nm

To study the discoloration of B.G dye, the UV-visible absorption spectra of (10 ppm) B.G dye solution at a pH=7.0 before and after treatment with photo-Fenton catalyst in the presence of 8W UVC are measured and presented in Figure 6.
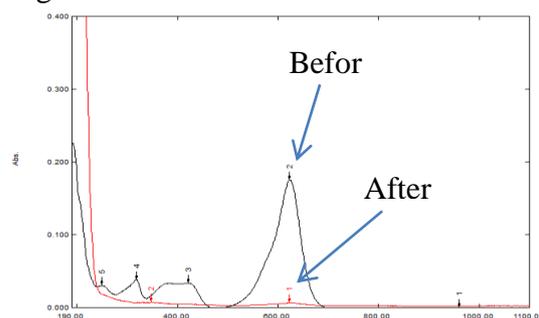
Fig. (6): UV-Visible Spectra of The 10 ppm of B.G Solution Before and After Treatment with Photo- Fenton Catalyst At pH=7.0 and 298.15K For 20 min.

To study the effect of initial dye concentration on the degradation efficiency, the experiments are carried out by using different initial concentration (10- 100) ppm at temperature 298.15K, pH= 7, and in presence ($2*10^{-4}$ M H_2O_2 + catalyst+ 8W UVA), Figure7 shows that the higher the initial dye concentration after 20 min leads to 90% percentage, while for 10ppm B.G concentration after 20 min reaches to 99.9%. This phenomenon might be due to the fact that the number of dye molecules is increased but the number of OH^- is still constant. On the other hand, with the increase in initial concentration of the dye, more dye molecules are adsorbed onto the surface of the catalyst, leading to a decrease in oxidation process. Figure (8) shows dark- Fenton without any UV light, in presence of ($2*10^{-4}$ M H_2O_2) ,and the catalyst at temperature 298.15K , pH= 7, the degradation of 10 ppm B.G dye after 20 min is 99% and for 100ppm dye is 90%. Similar results are obtained with photo- Fenton reaction. Figure (9) shows that in the absence of H_2O_2, with the catalyst at temperature of 298.15K , pH= 7, the degradation of 10 ppm B.G dye after 20 min is 95% and for 100ppm dye is 91%. This is indicates that H_2O_2 is important in diluting concentration of dye but isn't important in high B.G concentration. Figure (10) shows the effect of H_2O_2 concentration on the B.G dye degradation at temperature 298.15K, pH= 7, and (catalyst+ 8W UVA), 10 ppm of B.G dye degradation is 99% in case the concentration of H_2O_2 is $0.4*10^{-3}$M while the degradation percentage is 99.9% in case of using $3*10^{-3}$M H_2O_2 for high B.G dye concentration (100ppm). Low H_2O_2 concentration ($0.4*10^{-4}$M) leads to making the degradation percentage reach 89%.It is clear that $0.8*10^{-3}$M H_2O_2 is suitable to reach degradation percentage ranging (99- 100)% for B.G concentration 10,60,100ppm. Figure (11) shows the effect of pH on percentage degradation of B.G dye at temperature 298.15K, and in presence of ($2*10^{-4}$ M H_2O_2 + catalyst+ 8W

UVA).It is clear that the photo- Fenton degradation depends strongly on pH of the reaction medium, whereas the degradation percentage of B.G increases with increasing pH up to 7.0 and then percentage degradation of B.G decreases with increasing pH to pH= 14. The effect of temperature on the degradation of B.G dye is investigated in three different temperatures (298.15, 308.15, 318.15) K at the following condition pH=7, with different initial concentration (10, 20, 30, 40, 60, 80, 100) ppm of B.G. The results in Figure (12) show that, the degradation 10ppm of B.G decreases as temperature increases indicating an anti- Arrhenius relation. Then after increasing the temperature more than 318.15K, the R% stays with in the same level. Removal percentage for (20, 30, 40, 60, 80, 100) ppm increases when temperature increases until 320K the R% does not change for 320 to 330K. The degradation of B.G dye by Fenton is a first order reaction. This is determined from the slope of the linear plot of logarithmic remaining B.G concentration versus treatment time t as shown in the following Figure (13).
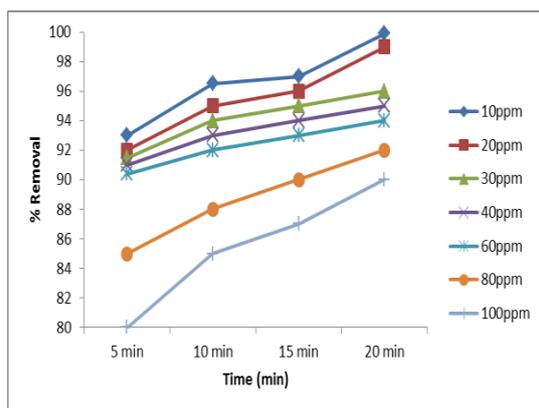
Fig.(7): Effect of Initial Dye Concentration on Degradation of B.G dye; at Temperature 298.15K, pH= 7, and (2*10^{-4} M H$_2$O$_2$ + Catalyst+ 8W UVA).
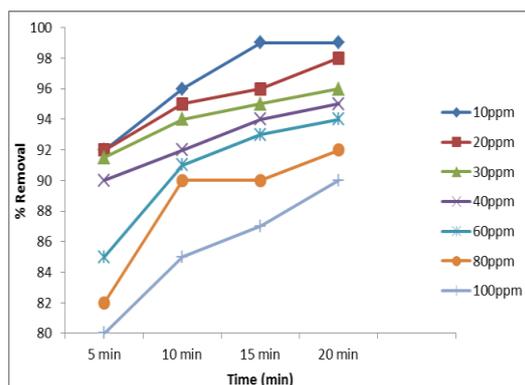
Fig. (8): %R Against Time for Different B.G dye Concentration with 2*10^{-4} H$_2$O$_2$ and without UV- light at 298.15
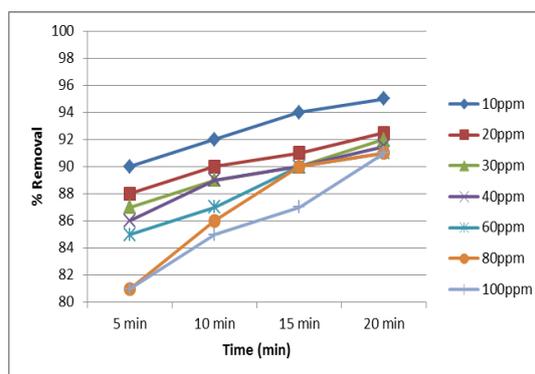
Fig. (9): %R Against Time for Different B.G Dye Concentration with UV- Light and without H$_2$O$_2$ at 298.15
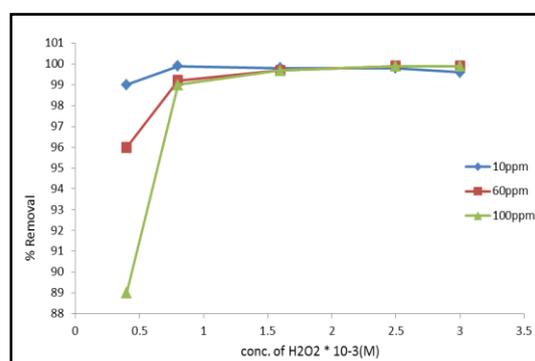
Fig. (10): Variation of R% with H$_2$O$_2$ Concentration for Different B.G Concentration in Presence of UV- Light and Catalyst at 298.15K and pH= 7
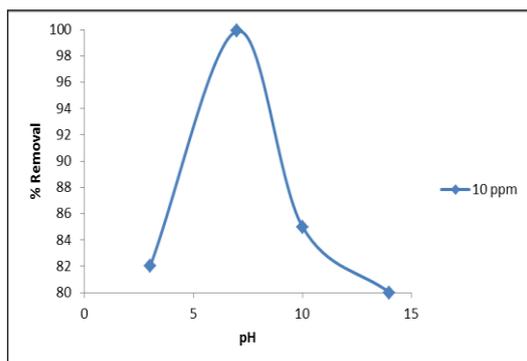
Fig. (11): pH Value and The % Removal
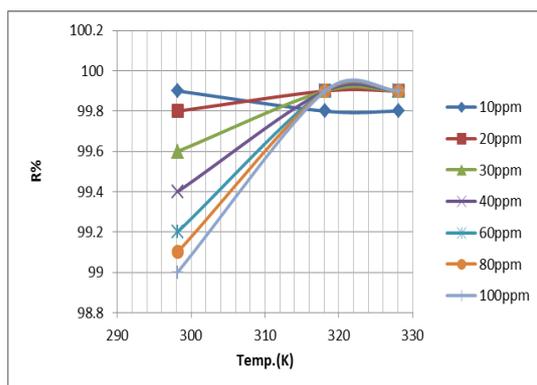
Fig.(12): %R against Temperature for Different B.G Dye Concentration after 20 Minutes
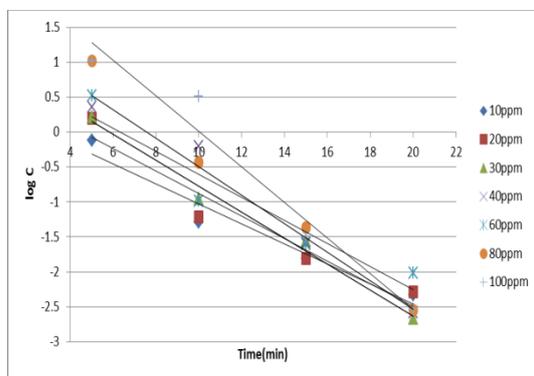
Fig. (13): The Relation between –logC and Time (min) at Temperature 298.15K

Conclusion:

Degradation of B.G dye is conducted by using bentonite clay- based Fe nanocomposite (Fe-B) film as a heterogeneous photo-Fenton catalyst in the presence of UVC light and H_2O_2. Under optimal conditions (pH= 7, $2*10^{-3}$M H_2O_2, and $1* 8W$ UVC), 99.9% degradation of B.G dye can be achieved in 20 minute. The Fe-B coated catalyst film could be used in the pretreatment of wastewater for an integrated system consisting of a photochemical reactor and biological reactor.

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دراسة حركية للتفكك الضوئي نوع (فنتون) المحفز لصبغة Brilliant Green باستخدام طين البنتونايت المزود بالحديد النانوي بسطح غير متجانس للتفاعل الضوئي المحفز

خلود عبد صاحب السعدي*　　　　شذى فاضل السعيدي**

حمدية حا تم جواد***

*قسم الكيمياء، كلية العلوم، جامعة بغداد.

**قسم الكيمياء، كلية العلوم، جامعة النهرين.

*** قسم الكيمياء، كلية العلوم للبنات، جامعة بغداد

الخلاصة:

يهدف هذا البحث الى دراسة التفكك الضوئي لصبغة Brilliant Green (.B.G) بالماء باستخدام تفاعل فينتون الضوئي (Fe^{+2} / H$_2$O$_2$/UV) وتفاعل فينتون (H$_2$O$_2$/Fe^{+2}) حيث تم دقائق نانوية من (الحديد-بنتونايت) كسطح فعال وقد طلي السطح الداخلي لخلية مختبرية. وقد اثبتت تحليل الاشعة السينية وجود SiO$_2$ (الكوارتز) بصورة رئيسية ووجود الحديد النانوي بهيئة Fe$_2$O$_3$ (الهيماتايت) البلوري. تم تقدير فعالية السطح المحضر (Fe-B) كعامل مساعد باستخدام الصبغة B.G ودرست قابليته على تكسير هذه الصبغة من المحلول بوجود ضوء الاشعة الفوق البنفسجية نوع C وبوجود بيروكسيد الهيدروجين. لقد تم متابعة محلول صبغة B.G ذات تركيز ابتدائي 10 اجزاء بالمليون عند رقم هيدروجين pH=7 وعند درجة حرارة 25 درجة مئوية ولوحظ ان 99.9% من الصبغة قد ازيلت او تكسرت خلال 10 دقائق.

ان للرقم الهيدروجيني pH تأثير كبير في التكسير الضوئي المحفز لصبغة B.6 كما تبين من خلال هذه الدراسة. ثم دراسة كل الظروف وثم الحصول على القيم المثلى للعمليتين (فينتون الضوئي)و(فينتون). ان عملية تجزء صبغة B.6 في المحلول المائي تتبع تفاعل المرتبة الاولى. وتفاعلات الفينتون الضوئي تؤدي الى كفاءة اكسدة عالية اكثر من مثيلاتها لتفاعل فينتون دون ضوء. وبالتالي تعتبر تفاعلات فينتون الضوئية عملية فعالة و اقتصادية يمكن ان تزيد من نسبة تكسير وازالة الملوثات بزمن تشعيع قصير.

الكلمات المفتاحية : عمليات الأكسدة المتقدمة ، فنتون ، فنتون الضوئي ، صبغة برلنت الخضراء.