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# A KINETIC STUDY FOR REMOVAL OF BISMARCK BROWN G BY ADSORPTION OVER PREPARED SUPPORTED $(Co, Ni)_3O_4/Al_2O_3$ SPINEL CATALYST

**EMMAN J. MOHAMMAD, SALIH H. KATHIM and ABBAS J. LAFTA***

Chemistry Department, College of Science, Babylon University, BABYLON 51002, IRAQ

## ABSTRACT

The supported co-catalyst $(Co, Ni)_3O_4/Al_2O_3$ was prepared via co-precipitation method. Two sets of these materials were prepared by calcination at two temperatures 500, and 600°C. Crystal structure of the prepared materials was investigated using powder X-rays diffraction (PXRD), and specific surface area (BET). The adsorption ability of the prepared catalyst $(Co, Ni)_3O_4/Al_2O_3$ was investigated by adsorption of Bismarck brown G dye (BBG) from simulated industrial wastewaters. Equilibrium adsorption isotherms and kinetics studies were investigated. The experimental data were analyzed according to Freundlich and Langmuir models of adsorption. The adsorption isotherms data were fitted well to Langmuir isotherm and the kinetic data were fitted very well with the pseudo-second-order kinetic model.

**Key words**: Spinel oxide, Dyes removal, Wastewaters, Bismarck brown G, Adsorption processes.

## INTRODUCTION

Dyes are organic molecules contain chromophores delocalized electron systems with conjugated double bonds, and auxochromes, electron-donating substituent's that intensify the color of the chromophore by altering the overall energy of the electron system. Auxochromes are usually such as $NH_2$, COOH, $SO_3H$ group. Large amounts of dyes are widely used in different types of industries, such as textile dye, cosmetic, paper printing, and pharmaceutical products[1,2]. According to presence of one or more azo groups (–N=N–), azo dyes can be divided into monoazo, diazo, and triazo classes and are found in different types such as acid, basic, direct, disperse, azoic and pigments. Azo dyes have the following basic structure[3].

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*Author for correspondence; E-mail: abbaslafta2009@yahoo.com

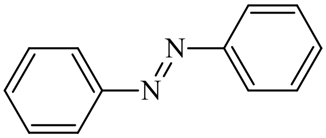

**Fig. 1: Basic structure of azo dye**

Bismarck brown G (BBG) is an azo dye, which has the molecular formula $C_{21}H_{24}N_8.2HCl$ and the molar mass is 461.39 g $mol^{-1}$. The IUPAC name of the Bismarck brown R is 4-[5-(2,4-diamino-5-methylphenyl) diazenyl-2-methylphenyl]diazenyl-6-methylbenzol-1,3-diamin. It is a dark brown solid, which is suitable for any fiber. Its solubility in water is 11 g $L^{-1}$ at 25°C and in ethanol is 9.8 g $L^{-1}$.[4] There are different ways that can be used to remove color textile effluents, including physical and chemical processes such as precipitation, and adsorption methods[5,6]. Generally, these dyes create many environmental pollution troubles by formation of carcinogenic materials and releasing toxic substances. Adsorption is the phenomenon of aggregation of large number of molecular species at the surface of catalyst. Adsorption process is completely different from absorption. While absorption means distribution of the substance throughout the bulk, adsorption happens essentially at the surface of the catalyst[7,8] .

There are two types of adsorption. Physical adsorption involves forces of molecular interaction which embrace permanent dipole, induced dipole moments, and quadruple attraction (Vander Waals adsorption). Physical adsorption is characterized by enthalpy changes that are small, typically in the range -10 to -40 kJ $mol^{-1}$, and heats of adsorption of 10- 40 kJ $mol^{-1}$. It takes place at low temperature below boiling point of adsorbate. This type of adsorption forms multilayer of adsorbate on adsorbent[9] also. Chemisorption, on the other hand, involves rearrangement of the electrons of the interacting gas and solid, with consequential formation and rupture of chemical bonds. Whereas heat of chemisorption are rarely less than 80 kJ $mol^{-1}$, and often exceed 400 kJ $mol^{-1}$, Chemisorption is that adsorption, which involves a chemical reaction between the adsorbate surface and new chemical bonds are generated at the adsorbent surface. Also chemisorption forms one layer of adsorbate on adsorbent. After the chemisorbed species combine by forming bonds with each other, the formed are desorbs from the surface [10].

The present work aims to study removal of BBG from textile industrial wastewaters by adsorption over prepared photocatalyst $Ni_3O_4.Co_3O_4/Al_2O_3$ and under applying different reaction conditions.

# EXPERIMENTAL

## Material and chemicals

### Chemicals

All the chemicals used in this study were used without any further purification. Aluminum nitrate, $Al(NO_3)_3.9H_2O$, cobalt nitrate hexahydrate $Co(NO_3)_2.6H_2O$, and nickel nitrate hexahydrate $Ni(NO_3)_2.6H_2O$ were obtained from BDH Company with purity 99.5, 97.9, and 99.9%, respectively. Sodium carbonate anhydrous, $Na_2CO_3$ was obtained from Gmbh with purity 99.9%. The absorbance of the supernatant liquid was measured at a wavelength of 468 nm, using UV-visible spectrophotometer (UV-1650PC Shimadzu, Japan). The dye used in this study was BBG. It has a molecular formula ($C_{21}H_{24}N8.2HCl$) and it was obtained from Al-Hilla Textile Factory.

### Catalyst synthesis

The supported co-catalyst was prepared by co-precipitation method. According to this method, 40% of $Co(NO_3)_2.6H_2O$, 40% of $Ni(NO_3)_2.6H_2O$ with 20% Al $(NO_3)$. $9H_2O$ were weighed accurately and dissolved in 400 mL of distilled water with a continuous stirring at room temperature under normal atmospheric conditions. The pH of the resultant mixture was adjusted using a digital pH meter to maintain pH at a required value. To this mixture, $Na_2CO_3$ (1M) was added drop wisely as a precipitating agent and the solution was kept at a temperature around (70-75$^o$C). Then the value of pH of the produced mixture was kept around 9.0. The resultant mixture was left for 2 hrs at same temperature with continuous stirring under air conditions. The obtained mixture was filtered of with Buchner filtration flask with a vacuum pump. The obtained solid was dried in an oven for overnight at approximately 120$^o$C. Then this material was calcinated at three different temperatures 500 and 600$^0$C at a heating rate of 10$^0$C/min for 4 hrs under normal air atmosphere[11].

## Catalyst characterization

### Powder X-ray diffraction (PXRD)

The crystal structure of prepared co-catalysts was investigated using powder X-ray analysis, Phillips X-ray diffraction with CuKα radiation (1.542 A$^0$, 40 KV, 30 MA), in the 2θ range, 10-80 degrees. XRD6000, Shimadzu, Japan.

### Surface area determination (BET)

The specific surface areas of the prepared co-catalysts were investigated by BET theory, using prep 060 and Gemini BET machine. According to this technique, 0.05 g of each sample was dried with flushing $N_2$ gas to remove pre-adsorbed gases in the sample. Then BET specific surface areas of the prepared co-catalysts were determined via adsorption of nitrogen at -196°C.

## Adsorption isotherm studies

In order to investigate adsorption isotherms for adsorption of BBG over the prepare catalyst, both Freundlich and Langmuir isotherms were investigated. A series of experiments were carried out using 30 ml, 50 ppm of dye aqueous solution with 0.2 g of the catalyst at 27°C for one hr After 60 min, the suspensions were filtered using a centrifuge, and the filtrates were analyzed for residual BBG by using UV-visible spectrophotometer at 468 nm using the equation:

$$q_e = (C_o - C_e) \times V)/W \qquad \ldots(1)$$

where $q_e$ is the amount of BBG adsorbed by the $Ni_3O4\text{-}Co_3O_4/Al_2O_3$ at equilibrium, $C_o$ and $C_e$ are the initial and final dye concentrations, respectively, V is the volume of solution (L), and W is the adsorbent weight (g).

## Adsorption isotherms of Bismarck brown G

## Langmuir adsorption isotherm

Langmuir adsorption isotherm suppose that adsorption takes place at specific homogeneous sites, monolayer adsorption[12]. The following equation is the Langmuir isotherm:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad \ldots(2)$$

where $q_m$ is the maximum amount of the BBG adsorbed per unit mass of the catalyst, and $K_L$ is the Langmuir constant .

## Freundlich adsorption isotherm

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems, Suppose that the adsorption on several layers (n) > 1[13]. Freundlich model is based on the distribution of an adsorbate between an adsorbent and the aqueous phases at equilibrium[14]. The following is the equation of the Freundlich isotherm –

$$\log (q_e) = \log K_F + \frac{1}{n} \log C_e \qquad \ldots(3)$$

where: $K_F$ and n are Freundlich constants.

### Adsorption kinetic modeling

To determine the rate of adsorption process two kinetic models were used. Pseudo-first order, and pseudo-second order models were used to analyze the kinetic data of the BBG adsorption onto the $Ni_3O_4$-$Co_3O_4/Al_2O_3$.

### The pseudo-first order kinetic model

The rate constant of adsorption was determined by using pseudo-first order equation given by Lagergren and Svenska[14]:

$$\ln (q_t - q_e) = \ln (q_e) - k_1 \qquad \ldots(4)$$

where: $q_e$ and $q_t$ (mg/g) are the amounts of the BBG adsorbed at equilibrium and at time t (min), respectively, and the adsorption rate constant *is* $k_1$ ($min^{-1}$).

### The pseudo-second order kinetic model

The pseudo-second order equation based on equilibrium adsorption is expressed in the following equation [15]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \ldots(5)$$

where: $k_2$ is the rate constant of the second order equation (g/mg min).

## RESULTS AND DISCUSSION

### X-ray diffraction (XRD)

From the obtained results of XRD patterns for the prepared catalyst, it was found that the crystallite structure was increased with elevation of calcination temperature at 500 and 600°C). Besides that, the particle size for these catalysts was increased with increase of calcination temperature. Also form these patterns, it can be seen that there were some deviation in the positions of the peaks and spaces - d for standard values by matching with

Joint Committee on Powder Diffraction Standards (JPCDS)[16]. This deviation is acquired by influencing between oxides. XRD patterns for the prepared catalysts are shown in Fig. 2.

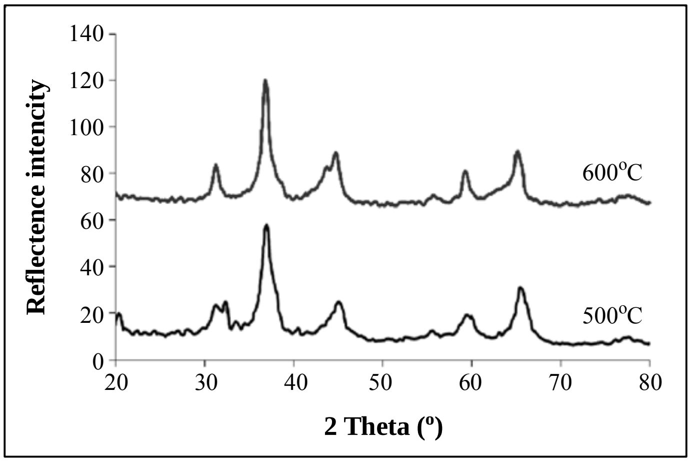

**Fig. 2: X-ray patterns for the prepared catalyst after calcination at different temperatures 500 and 600°C**

## Surface area determination (BET)

The results of pore volume and porosity of the prepared catalysts are shown in Table 1. From these results, it was found that the porosity was increased with increase the calcination temperature due to the effect of volatilization of the water and gas molecules that occur at high temperature. Also it was found that the BET surface areas and pore size were decreased with increase the calcination temperature. This is probably because of the effect of sintering processes that occur at high calcination temperature[17].

**Table 1: BET surface area, and pore volume of the catalyst and porosity**

| Calcination temperature ($^0$C) | Porosity (%) | Pore volume (cm$^3$/g) | BET (m$^2$/g) |
|---|---|---|---|
| 500 | 64.460 | 1.185 | 163.235 |
| 600 | 65.120 | 1.174 | 123.174 |

## Activity of the prepared catalyst: Adsorption

The effect of adsorption of the prepared catalyst in (500, 600°C) on removal BBG was investigated after 60 min. It was found that the removal efficiency of the prepared catalyst was higher at 600°C than catalyst that prepared at 500°C. This probably arises from a high porosity for the catalyst calcinated at 600°C in comparison with that calcinated at 500°C. The results of BBG removal in these two cases are shown Fig. 3.

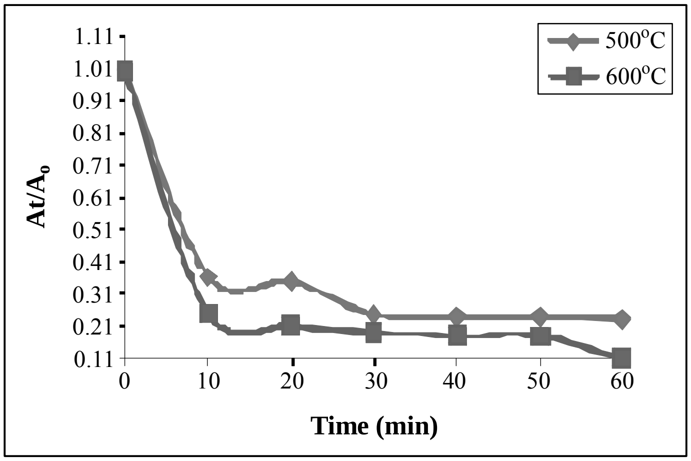

**Fig. 3: Removal of BBG over prepared catalyst under calcination at different temperatures 500, 600°C**

## Effect of adsorption time on the removal BBG dye

The effect of adsorption time on removal BBG was investigated by using 0.2 g of catalyst and 30 mL of 50 ppm dye solution, It was found that the removal efficiency of dye after 60 min was 86.6%.The results are shown in Table 2 and Fig. 4.

**Table 2: The remaining percentage of BBG after 60 min of the adsorption**

| Time (min) | $A_t/A_o$ of BBG |
|---|---|
| 0 | 1 |
| 10 | 0.013 |
| 20 | 0.011 |
| 30 | 0.005 |
| 40 | 0.003 |
| 50 | 0.001 |
| 60 | 0.001 |

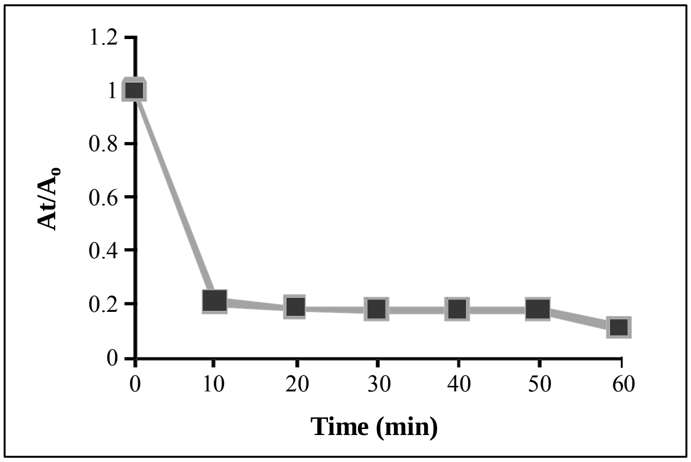

**Fig. 4: The remaining percentage of adsorption BBG over the catalyst**

## Adsorption isotherms for dye adsorption over the catalyst

Adsorption isotherms were studied using Langmuir and Freundlich equilibrium models. These isotherms are shown in Figs. 5 and 6, respectively. Table 2 shows values of Langmuir and Freundlich adsorption isotherms.

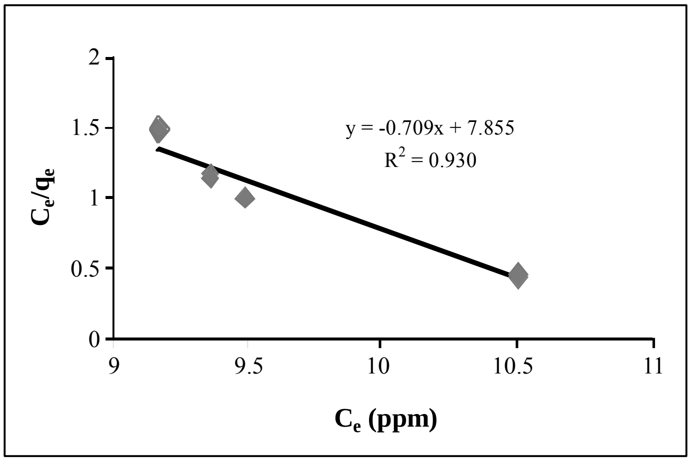

**Fig. 5: Langmuir adsorption isotherm for adsorption of BBG on the prepared catalyst**

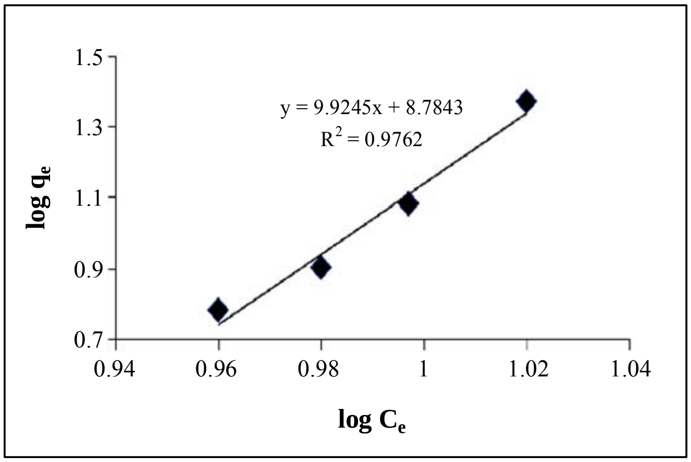

**Fig. 6: Freundlich adsorption isotherm for adsorption of BBG over the catalyst**

From results summarized in Table 3, it can be seen that the value of the correction factor ($R^2$) that are obtained from Langmuir model is lower than that for Freundlich isotherm. This means that, this process agrees with Langmuir model. The value of n that represents the number of adsorbed layers is 0.1. In this case, adsorption processes followed Langmuir adsorption isotherm[18].

**Table 3: The adsorption constants of the Langmuir and Freundlich isotherms**

| Type of isotherms | Parameters | Values |
|---|---|---|
| Langmuir | $Q_m$ | 1.074 |
| | $K_L$ | 0.118 |
| | $R^2$ | 0.930 |
| Freundlich | $K_F$ | 2.172 |
| | n | 0.100 |
| | $R^2$ | 0.976 |

## Adsorption kinetics

Through the results shown in the Table 4, it is found that the value of the correction factor for the pseudo second order kinetic model (0.9979-0.9939) is higher than the value of the first false correction coefficient. Through this result, it is clear that the dye adsorption process of BBG follows the pseudo-second order kinetic model.

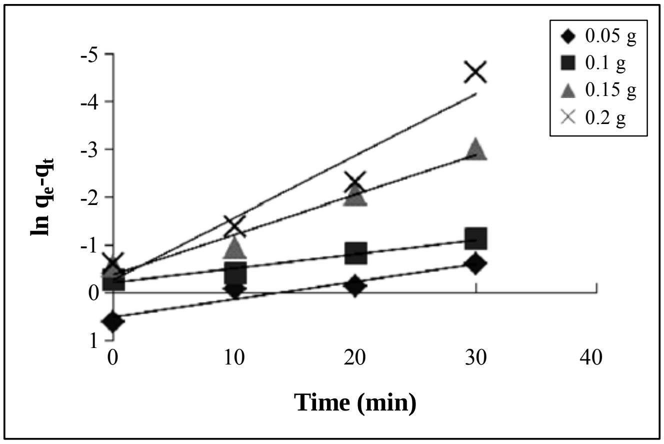

**Fig. 7: The pseudo-first order kinetic model**

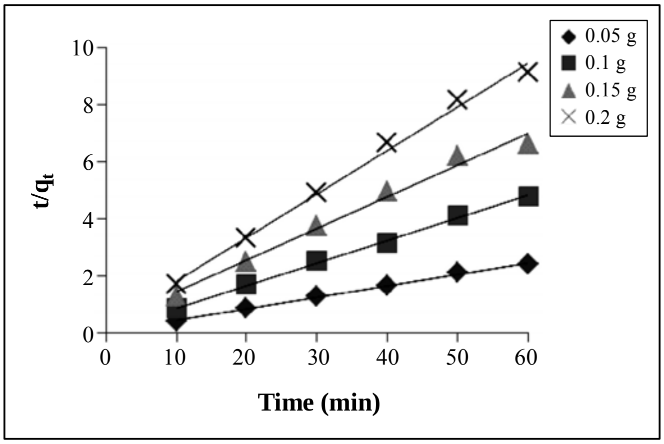

**Fig. 8: The pseudo-second order kinetic model**

**Table 4: The adsorption parameters for RY145 adsorption onto $Ni_3O_4$-$Co_3O_4$/$Al_2O_3$**

| Wt (g) | Pseudo first order model | | | |
|---|---|---|---|---|
| | $q_{e,exp}$ (mg/g) | $q_{e,cal}$ (mg/g) | $K_1$ ($min^{-1}$) | $R^2$ |
| 0.05 | 23.7 | 1.648 | 0.037 | 0.9086 |
| 0.10 | 12.15 | 1.236 | 0.03 | 0.9697 |
| 0.15 | 8.06 | 1.456 | 0.0838 | 0.9762 |
| 0.20 | 6.12 | 1.322 | 0.1293 | 0.9276 |

Cont…

| **Wt (g)** | **Pseudo second order model** | | | |
|---|---|---|---|---|
| | **$q_{e,exp}$ (mg/g)** | **$q_{e,cal}$ (mg/g)** | **$K_2$ (g/mg min)** | **$R^2$** |
| 0.05 | 23.7 | 24.39 | 0.502 | 0.9979 |
| 0.10 | 12.15 | 12.5 | 0.500 | 0.9987 |
| 0.15 | 8.06 | 8.72 | 0.505 | 0.9870 |
| 0.20 | 6.12 | 6.42 | 0.502 | 0.9939 |

## CONCLUSION

As the prepared catalyst has high porosity at 600°C, so it used in the removal of Bismarck brown G dye by adsorption at pH = 3, catalyst conc. = 0.2 g $L^{-1}$, temperature = 27°C, and adsorption time of 60 min. The equilibrium adsorption isotherms from the obtained results adsorption isotherms, it was more fitted with the Langmuir adsorption model, and the value of the correction factor for the pseudo second order kinetic model was higher than the value of the first false correction coefficient the pseudo-first order kinetic model. So the adsorption process of BBG follows the pseudo-second order kinetic model.

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