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# Removal of Methylene Blue Dye from Aqueous Solution Using Activated seed shell of Balanites Aegyptiaca L Delile

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**Abstract** In the present study, the removal of the methylene blue dye (MB) from the water solution was investigated using Balaines Aegyptiaca powder as an adsorbent. The seeds of Balaines Aegyptiaca were collected from Sebha, Libya. Factors affecting the removal processes such as initial concentration, contact time, absorbent dose, temperature and solution pH were probe. The results showed that the state of equilibrium was reached in two hours. Maximum removal of 63.59% was achieved at pH of 5.90, contact time of 2 hours, 100 mg/l of MB and room temperature. The efficiency of adsorption and removal ratio was reduced with temperature increase from 20 ° C to 40°C and increased with increase in the absorbed dose. Increased efficiency and dehydration were observed increasing the concentration of sodium chloride with a grade of( 1 to 4M of NaCl )to approximately (90%) The results in this study indicate that the powder of the bark Balaines Aegyptiaca seeds.

**Keywords:** removal, adsorption, Balaines aegyptiaca L seed shell powder, Methylene blue.

# إزالة صبغة المثيلين الأزرق من محلول مائي باستخدام قشرة بذرة نبات الهجليج المنشط

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**الملخص** في هذه الدراسة، دراسة إزالة صبغة المثيلين الأزرق من المياه الملوثة باستخدام مسحوق قشور بدرة نبات الهجليج كمادة مازة. جمعت بذور نبات الهجليج من مدينة سبها، ليبيا. لقد تم دراسة العوامل التي تؤثر على عمليات الإزالة على سبيل المثال التركيز الصبغة وزمن الاتصال بين الصبغة والمسحوق وكمية المادة المازة ودرجة الحرارة والأس الهيدروجيني. أظهرت النتائج أنه تم الوصول إلى حالة التوازن خلال ساعتين من بداية التلامس. وكانت أقصى إزالة 63.59 ٪ عند درجة الحموضة من 5.90 وزمن الاتصال ساعتين و100 ملغ / لتر من الصبغة ودرجة حرارة الغرفة. وبصورة عامة انخفضت كفاءة الادمصاص ونسبة الإزالة مع زيادة درجة الحرارة من 20 إلى 40 درجة مئوية ولوحظ زيادة في كفاءة الادمصاص مع زيادة كمية المادة المازة. كما لوحظ أيضا زيادة كفاءة الادمصاص والإزالة للصبغة من المحاليل المائية بزيادة تركيز كلوريد الصوديوم من (1 إلى M4 من كلوريد الصوديوم) إلى ما يقرب من (90 ٪) وتشير النتائج في هذه الدراسة إلى أن مسحوق بذور نبات الهجليج دو كفاءة عالية للإزالة.

**الكلمات المفتاحية:** إزالة، امتزاز، مسحوق قشور بدرة نبات الهجليج، أزرق المثيلين.

## 1. Introduction

Dyes are applied in various industries such as leather, textile, paper, rubber, cosmetic, plastic, pharmaceutical and food industries. However, those dyes are basically natural or synthetic organic compounds that can use to bind to the surfaces or fabrics to provide colours **[1]**. Those dyes can be discharged directly into the ecosystem from manufacturing operation and associated industries leading to pollute wastewaters and water streams, washing, bathing and drinking **[2].** Moreover, all of those dyes are found to cause allergy, dermatitis, skin irritation, cancer and mutations in humans. These issues on environmental concern from many produced dyes has been raised especially their entering in the surface water, which affect the aquatic plants reducing sunlight to inhibit the growth of bacteria **[3]**. Therefore, the removal of discharged dyes from industrial processes is an important matter.

However, one of the most used dyes in the world is Methylene blue (MB), which also knowns as cetylpyridinium chloride and a thiazine dye. The MB dyeis used as medication to treat methemoglo binemia especially at or symptoms despite oxygen therapy and for cyanide poisoning antennary tract infections. Also there are a common side effects using MB including headache, vomiting, confusion, shortness of breath, and high blood pressure **[4]**. However, the MB dyes are usually discharged from laboratory usages and manufacturing operation in industries into the water ecosystem with large scale quantities. The removal MB dyes from ecosystem environment needs to pay a great concern. Many treatment methods have been applied for removing discharged MB dyes from aqueous solutions. One of the most preferable process is adsorption processes for the treatment of the wastewater due to its inexpressive, simple design and easy operation, less energy intensiveness, no effect by toxic substances and high quality of the treated effluents particularly for well-designed sorption processes **[5]**. Activated carbon is the most widely used as adsorbents for removing organic and inorganic dissolved pollutants from water and wastewater due to their high adsorptive capacity and inexpensive preparation processes to produce a great surface area, a high micro-porosity and presence of surface functional groups of activated carbon **[6]**. Recently, the demand of activated carbons from natural products has increased significantly for water-purifying agent the water pollution worldwide **[7]**. However, it was found that the adsorbent such as Banalities aegyptiaca L shells was utilized to remove heavy metals like Ni (II) and copper Cu (II) ions from an aqueous solution **[8]**. In this research, the removal of MB dye onto the surface of Banalities aegyptiaca L shells, BALS, was investigated. The BALS is native plant raised at Africa and parts of the Middle East, which classified either as a member of the Zygophyllaceous or the Balanitaceaee.

## 2. Materials and method

### 2.1. Chemicals and Instruments

The chemicals were used in this study methylene blue, phosphoric acid(0.1M), Sodium hydroxide (0.1M), Hydrochloric acid (0.1M) and all of these chemicals were used without further purification. The instruments which were used in this study: pH meter Thermo, Infra-red spectrometer(IR200), UV-Vis spectrophotometers (Jenway model 6305).

### 2.2. Sample preparation

Banalities aegyptiaca L shells, BALS, were collected from Sebha City, Libya in summer session 2017. They were then sun dried for one day before grinding using the hand propulsion machine. The water was rinsed with distilled water several times was washed with hydrochloric acid (HCl) to remove the impurities and wash with phosphoric acid($CH_3COOH$) to remove the alkali Weight was used increase the surface area. The milled substances were washed with distilled water. The dry BALS was rinsed with 1 HCl on order to remove water soluble impurities and then kept in 0.1Mof NaOH solution for 24 hrs in order to remove lignin. The mixture was put in 0.1Mof $CH_3COOH$ in order to remove alkalinity developed by NaOH. The residual materials of BALS were washed several times with distilled water till the wash water became colourless and pH of the solution was neutral. The BALS was chemically activated using NaCl and dried at 105°C for two hours till the weight was constant and the left material was physically activation at 500°C.

### 2.3. Mathematical adsorption models

The removal percentage, adsorption capacity at time $t$ ($q_t$) and adsorption capacity at equilibrium ($q_e$) were calculated using the equations**[9]**:

$$q_t = \frac{C_0 - C_t}{m_s} \times V \quad \text{..................(1)}$$

$$q_e = \frac{C_0 - C_e}{m_s} \times V \quad \text{.................(2)}$$

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \quad \text{.................(3)}$$

Where:$C_0$ and $C_e$ (mg/L) are the initial and the final concentrations of adsorbates in flasks, respectively,$C_t$(mg/L) is the concentrations of adsorbates at time t. V is the volume of the solution (L) and $m_s$ is the mass of dry adsorbent used (g)Where:$q_e$ and $q_t$ are the amounts of MB (mg/g) at equilibrium and at time t, respectively, and R% removal.

### 2.4. Experimental processes

The effect of adsorbent dosage BALS was studied at different doses (0.005, 0.01, 0.02, 0.03, 0.04, 0.05,0.07 g) by adding into 50 ml flasks with 20mL of 100 mg/L MB solution. The effect of contact time was studied by adding 100 mg of BALS into 50 ml flasks of 20 mL of 100 mg/L MB. The samples were then taken for different contact times in the range from 0 to 120 min. The effect of the pH solution was studied by changing from 3 to 11 by adding drops of 0.1M HCl or 0.1M NaOH into 20 ml of 100 mg/L MB solution and 0.01 g of adsorbent dosage. The samples were then taken after 2 hrs. The effect of initial concentration was also studied by adding 0.01 g of BALS to each 20 ml of MB at different temperature (20, 30 and 40°C). All the experimental was then agitated at 300 rpm for 120 min. The concentration of MB left in solutions was measured by using the absorption by UV-Vis spectrophotometer (Jenway model 6305) at 662 nm.

## 3. Results and Discussion

### 3.1. Effect of adsorbent dosage

**خطأ! لم يتم العثور على مصدر المرجع.** shows the effect of adsorbent dosages on the adsorption processes of BALS and MB. It was noted that the percentage removal was increased with increasing of the adsorbent dosage of BALS. This could be due to the increase in the binding sites available for MB on the surface of BALS. Also, it was found that the $q_e$ values were decreased with increasing of adsorbent dosage of BALS, which could be due to the active sites on the surface of the adsorbent material of BALS were saturated by MB during the adsorption processes.

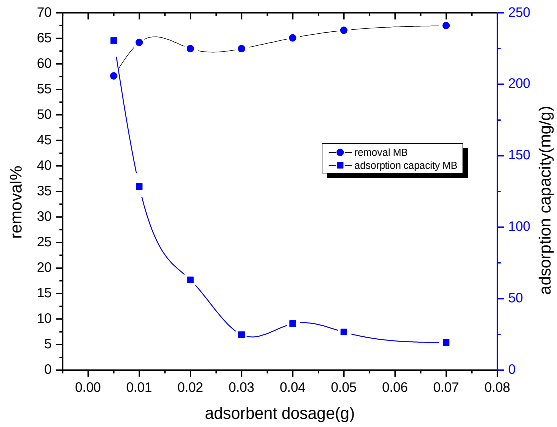


**Figure 1.** Effect of adsorbent dosages on the removal and adsorption capacity of BASS under

condition Co 100 mg/g, 300 rpm,120 minute,20ml, pH=5.90, and room temperature

### 3.2 Effect of contact time

Figure 2 shows the relationship between the contact time and R% and $q_e$ on the adsorption processes of BALS and MB. The percentage removal of MB onto BALS surface and $q_e$ were increased with increasing the contact time. The highest percentage removal was achieved at two hours 63.59% and the qe of the absorbent substance was 127.18 mg/g. The contact time was chosen at 120 min due to no change on removal after this point. This could be also considered as physical adsorption of the adsorption processes of BALS and MB due to requiring a short period of time for the equilibrium between the BALS and MB dye **[10]**.

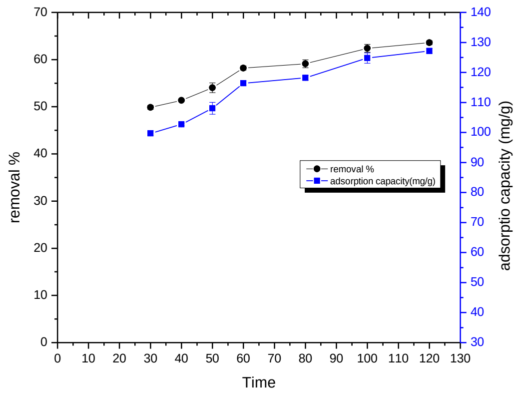


**Figure 2.** Effect of time contact time on the removal and adsorption capaity under conditions Co 100 mg/L, 300 rpm, dosag0,01g, 20ml, pH=5.90, roon temperature.

### 3.3. Effect of solution pH

**Figure 3** shows the effect of pH on the adsorption processes of BALS and MB. The pH solutions were changed from 3 to 11 of 0.01 g BALS and 100 mg MB at room temperature. It was found that the R% and $q_e$ were increased as the pH was raised from 7 to 11 and from 7 to 4.At low pH, the maximum value of $q_e$ obtained was 5.90. At higher pH values more than 7,the increase of the removal was also reported, which could be due to the strength of interaction between the positive dye with a negative charge of adsorbent surface**[11, 12]**.

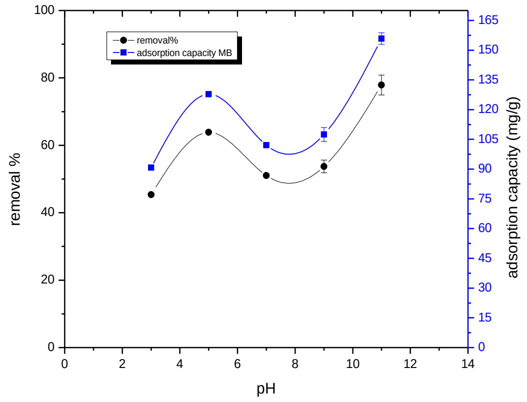


**Figure 3.** Effect of pH on the removal percentage andadsorption capacity under condition Co 100 mg/L, 300rpm, 120 min, dosag 0.01g, 20ml, room temperature

### 3.4. Effect of initial MB concentration

خطأ! لم يتم العثور على مصدر المرجع. shows the effect of the initial MB concentration of dye on the adsorption processes of BALS and MB at constant weight of adsorbent, BALS. It was found that the percentage removal was decreased with increased initial MB concentration and temperature. This could be due to the dependent on the relationship between the MB concentration and the available binding sites on an BALS surface**[13, 14]**.

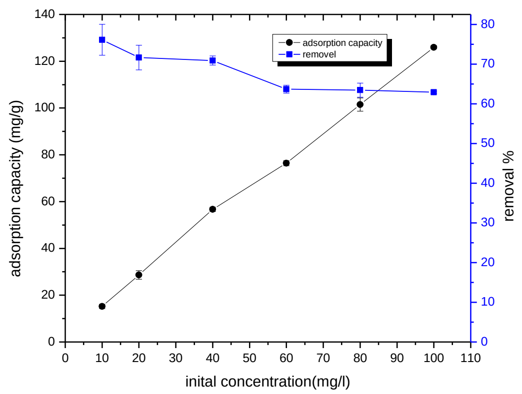


**Figure 4.** of initial concentration on removal and adsorption efficiency under condition dosage 0.01 g, 20ml, pH=5.90, 300 rpm, 120min, room temperature

### 3.5 Effect of temperature

The solution temperature of the adsorption processes is an important factor that has an effect on the adsorption process (R%)[14, 15]. The effect of the solution temperature on the adsorption processes of BALS and MB was studied at different temperatures (20-40C$^0$) at pH of 5.90, 0.01g of BALS and contact time 120 min as shown in Figure 5. It was found that all the percentage removal was reduced by increasing the temperature (20-40C$^0$). It is clear that the adsorption processes of BALS and MB is an exothermic process [16].It was also noted that the increase in temperature leads to a weakening of the absorption forces between the MB dye and the BALS surface [17, 18]. This could be used for desorption and separation MB from the surface of BALS. This indicates that the process of adsorption is favourable at low temperature.

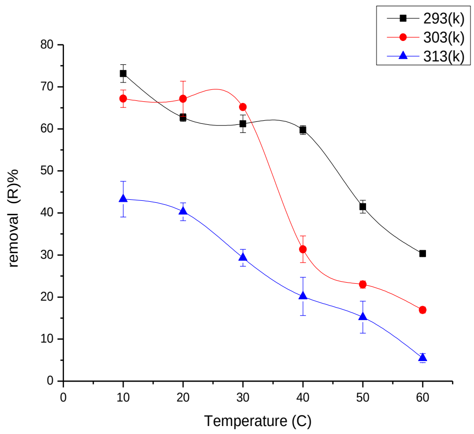


**Figure 1**. Effect of temperature on removal percentage the adsorption processes of BALS and MB under condition Co 100mg/g, dosage 0.01 g, 20ml, pH=5.90, 300rpm, 120min

### 3.6 Effect of NaCl addition

The effect of NaCl concentration was also investigated which to study the effect of interference ions present on ecosystems on the adsorption processes at different concentrations[15].The dosage of NaCl were added from 1 to 4mg.It was found that the absorption capacity of MB and BALS was increased with increasing the concentration of NaCl. This could be due to the fact that the increase in ionic strength by increasing the Na ions on solution.

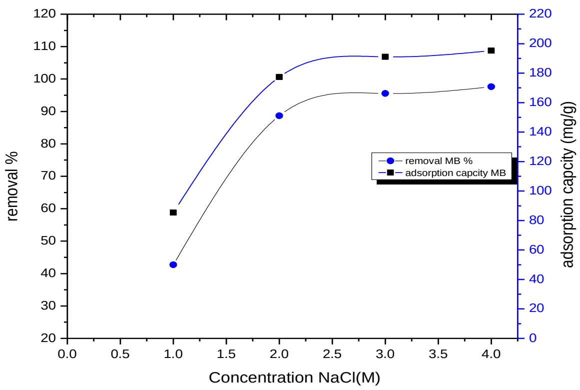


**Figure 6.** Effect of salt addition on the adsorption processes of BALS and MB (rpm: 300; pH: 5.90at MB at Temperature room at C0 100 mg/l

### 3. Conclusion

In the present research, the removal of MB from aqueous solutions was reported by using activated BALSS. The adsorption behaviour was testes by using the contact time, adsorbent dosages, pH, MB concentration and temperature. It was found that the removal percentage increased with increasing adsorbent dosage, pH solution and decrease with increasing initial concentration and temperature. The findings in this study that BALS could be used as adsorbent to remove MB from aqueous solutions.

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**References**

[1]- Chowdhury, M.A. and K.J. Fatema, *Review of Renewable Biosorbent from Coir Pith Waste for Textile Effluent Treatment.* International Journal of Textile Science, 2016. **5**(6): p. 132-140.

[2]- Demirbas, A., *Heavy metal adsorption onto agro-based waste materials: areview,* . Journal of hazardous materials, (2008). **157(2)**:: p. 220–229.

[3]- Seow, T.W.a.L., C. K. , *Removal of dye by adsorption: A review, International* Journal of Applied Engineering Research, . (2016). **11(4)**:: p. 2675–2679.

[4]- Petzer, A., Harvey, B. H., Wegener, G. and Petzer, J. P *Azure b, a metabolite of methylene blue, is a high-potency, reversible inhibitor of monoamine oxidase, Toxicology and applied pharmacology.* . (2012). . **258(3)**:: p. 403–409.

[5]- Vaishnav Veined, D.K., Chandra Suresh and Lal Madan,, *Adsorption Studies of Zn (II) ions from Wastewater using Calotropis procera as an Adsorbent.* Research Journal of Recent Sciences 2012. **1**: p. 6.

[6]- Nwabanne, J.T.a.I.P.K., *Preparation of Activated Carbon from Nipa Palm Nut: Influence of Preparation Conditions.* Research Journal of Chemical Sciences, 2011. **1(6)**: p. 6.

[7]- Ansari Khalkhali R., O.R., *Adsorption of Mercuric Ion from Aqueous Solutions Using Activated Carbon.* Polish Journal of Environmental Studies, 2005. **14(2)**: p. 3.

[8]- Chen, J.P., Yoon, J.-T. and Yiacoumi,, *S Effects of chemical and physical properties of influent on copper sorption onto activated carbon fixed-bed columns, Carbon.* . (2003). **41(8):** : p. 1635–1644.

[9]- Hussin, Z.M., et al., *Methylene blue adsorption onto NaOH modified durian leaf powder: isotherm and kinetic studies.* American Journal of Environmental Engineering, 2015. **5**(3A): p. 38-43.

[10]- Mohamed, E.F., *Removal of organic compounds from water by adsorption and photocatalytic oxidation*. 2011.

[11]- Rahim, A.A. and Z.N. Garba, *Efficient adsorption of 4-chloroguiacol from aqueous solution using optimal activated carbon: Equilibrium isotherms and kinetics modeling.* Journal of the Association of Arab Universities for Basic and Applied Sciences, 2016. **21**: p. 17-23.

[12]- Kushwaha, A.K., N. Gupta, and M.C. Chattopadhyaya, *Removal of cationic methylene blue and malachite green dyes from aqueous solution by waste materials of*

*Daucus carota.* Journal of Saudi Chemical Society, 2014. **18**(3): p. 200-207.

[13]- Jagung, P.T., *Removal of Zn (II), Cd (II) and Mn (II) from aqueous solutions by adsorption on maize stalks.* Malaysian Journal of Analytical Sciences, 2011. **15**(1): p. 8-21.

[14]- Erhayem, M., et al., *Isotherm, kinetic and thermodynamic studies for the sorption of mercury (II) onto activated carbon from Rosmarinus officinalis leaves.* 2015. **6**(01): p. 1.

[15]- Tahir, M.A., H.N. Bhatti, and M. Iqbal, *Solar Red and Brittle Blue direct dyes adsorption onto Eucalyptus angophoroides bark: equilibrium, kinetics and thermodynamic studies.* Journal of Environmental Chemical Engineering, 2016. **4**(2): p. 2431-2439.