THE REMOVAL OF METHYLENE BLUE DYE AS ORGANIC POLLUTANT FROM AQUEOUS SOLUTIONS BY USING SOME LOW COST NATURAL MATERIALS

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Abstract

Rice straw as a low cost by-product and hen egg shell as a natural waste were investigated for their efficiency toward removing methylene blue (cationic dye) as an organic pollutant, from aqueous solutions. The effect of contacting period between the investigated adsorbents and the experimental dye, as well as adsorbents dosage and initial dye concentration were examined for the highest removal efficiency percentage. Obtained results revealed that the optimum contacting periods for rice straw (RS) and egg shell powder (ESP) were 100 and 15 minutes respectively. Obtained results indicated that 1.5 g/l of RS and 1 g/l of ESP were the optimum dosages. At the end of the study, it's obtained that as the initial dye concentration increase the amount of MB adsorbed per the unit weight of the adsorbent was decreased. The equilibrium adsorption behavior was examined by applying Langmuir and Freundlich adsorption isotherm models. The Langmuir isotherm parameters X m and K l and the Freundlich isotherm parameters K f and n were determined from the adsorption equilibrium data for the various samples. Correlation coefficients were also determined. Obtained results revealed that the equilibrium adsorption data fitted well to the two models. Obtained results and their statistical manipulation proved that both RS and ESP could be potentially considered for removing MB dye from its aqueous solution.

INTRODUCTION

Synthetic dyes are extensively used by industries including dye houses, paper printers, textile dyers 'colour photography and as additives in petroleum products (Zollinger, 1991and Selvam *et al.*, 2003). The effluents of these industries are highly colored and disposal of these wastes into the environment can be extremely deleterious. Their presence in watercourses is aesthetically

unacceptable and may be visible at concentration as low as 1 ppm (Zollinger, 1991). Moreover, they may also affect photosynthetic activity in aquatic systems by reducing light penetration (Mahony *et al.*, 2002).

Several workers have examined toxicity of dyes and textile wastewaters on fish in relation to their mortality (Rana and Raizada, 1999 and Karanjkar *et al.*, 2000), and changes in RBC counts (Goel *et al.*, 1981) and their morphological abnormalities (Murugesan *et al.*, 1989).

In Egypt the problem of color removal from textile wastewater has been considered to be of great importance because of the need to satisfy the increasing demand for water for various uses. For this reason, a national effort has been launched to deal with this problem using natural, local adsorbents. Investigations have been undertaken to determine whether cheap commercially available materials hold promise in the treatment of wastewater. In spite of the presence of a huge number of dyestuffs which are widely used in dyeing processes, little data are available about their removal from dyeing wastewater. Adsorption is used in industrial wastewater treatment to remove organic materials such as color, phenols, detergents, and other toxic or non-biodegradable (El- Sherbiny *et al.*, 2009).

Due to low biodegradability of dyes a conventional biological treatment process is not very effective in treating a dye wastewater. It is usually treated by physical and/or chemical methods (Garg *et al.*, 2003). Although these treatment methods are efficient, they are quite expensive and have operational problems (Garg *et al.*, 2003 and Kapdan *et al.*, 2000).

Adsorption of the molecules onto various adsorbents is an ideal option for de-colourization, which is evidenced by the effectiveness of adsorption for various dye types (Kapdan *et al.*, 2000 and Porter *et al.*, 1999).

Rice cultivation produces large quantities of straw waste, ranging from 2 to about 9 tons/ha globally (Parr *et al.*, 1992). Rice is one of the most abundant crops in Egypt, 2 million feddans (EEAA, 2008) with an average production of about 6.12 million tons per year and 9.5 tons per hectare in 2005

(FAO, 2006). In Egypt, processing of rice in the River Nile Delta yields large amounts of rice straw as residue. About 20% was used for other purposes such as ethanol, paper, and fertilizer production as well as fodders (El-Gammal and Shakour, 2001) and the remaining part was left in the fields for burning within a period of 30 days to quickly get rid of leftover debris. The resulting emissions significantly contribute to the air pollution called the "Black Cloud" (Keshtkar and Ashbaugh, 2007). While rice straw has large potential to be used for controlling water quality as reported by Shahabuddin (2012).

William and Owen (1995) reported that egg shell considered a promising material to serve as an adsorbent agent, because its chemical composition and its porous nature. The principal component of the shell is calcium carbonate which comprises more than 90% of the material (William and Owen, 1995; Kuh and Kim, 2000 and Stadelman, 2000).

Methylene blue, a basic dye, is a heterocyclic aromatic chemical compound with a diversity of different fields, including the dyeing of silk, leather, paper, wool and cotton, and the production of ink and copying paper, as well as the quality control test of concrete and mortar (Berneth, 2003) On the other hand, it has been used as an effective therapeutant and antibacterial to protect newly laid fish eggs from being infected by fungus or bacteria in the aquacultural industry (Tacon and Forster, 2003). Therefore, it is necessary to limit the potential negative impacts of aquacultural farm discharges on environmental quality, and also maintain high surface water quality through a recirculating aquaculture system during cultivation of fish.

The choice of methylene blue as adsorbate is due to its known strong adsorption onto solids (Özer and Dursun, 2007).

The present work aims to investigate the efficiency of row rice straw and egg shell as low cost natural bi-products for removing methylene blue dye as an organic pollutant from aqueous solutions.

MATERIALS AND METHODS

Methylene blue (MB) Preparation and Determination:

In this experiment, Methylene blue (MB) dye was investigated for its removal from its aqueous solution. MB is a heterocyclic compound, dark green powder with the chemical structure: $C_{16}H_{18}CIN_3S$. MB solution was prepared by dissolving MB powder in distilled water to prevent or at least minimize possible interference. The dye was stirred until it was completely dissolved. A stock solution of the dye was prepared by dissolving 1gram of dye in 1000 mL distilled water to make a stock solution of 1000 mg/L. Then, the experimental solution was prepared by diluting definite volume of the stock solution to get the desired concentration. A series of standards with different dye concentrations were prepared, while distilled water was used as a blank (0 mg/L). The blank and the standards were introduced into the UV-visible spectrophotometer at a wavelength of 664 nm and the absorbance reading of the blank and each standard were recorded.

Adsorbents preparation:

Rice straw (RS) preparation:

Rice straw remained as a waste after rice harvesting, gathered from the surrounding fields and prepared through the following steps: 1- washed by distilled water. 2- Sun dried for several days until complete dryness. 3- Cut to small pieces. 4- Passed through very tight mesh sieve to obtain particles smaller than 1mm. 5- dried in an oven at 60°C until constant weight. 6- Kept in plastic–stopper bottles which preserved in desiccators to minimize contact with humidity until use.

Egg shell powder (ESP) preparation:

Natural hen eggs were washed with tap water several times then airdried and incubated in hot air oven at 40 °C for 30 minutes (to prevent denature of egg shell protein component which happen at temperatures higher than 40 °C). Consequently, egg shells were ground to a powder in a grinder, and sieved to obtain between 60-100 mesh (0.25-0.104 mm) size particles (Arunlertaree *et al.*, 2007).

Effect of Contact Time:

0.5 g of each of the investigated adsorbent materials (RS and ESP) was added separately to 500 ml of MB dye solution with concentration of 100 mg/L at room temperature. The mixture was stirred continuously with a magnetic stirrer. The samples were then taken at different contact periods (2, 5, 10, 15, 20, 40, 60, 80, 100 and 120 minutes), filtered and the dye residues in each sample were determined with UV-VIS Spectrophotometer. The removal efficiency of each adsorbent substance at different tested contact periods was investigated.

Effect of Adsorbent Dosage:

The optimum dose of each of the investigated adsorbent materials, was determined by mixing various amounts of RS or ESP (0.2, 0.4, 0.6, 0.8, 1.0 and 1.5 g) into 1000 ml of six 100 mg/L MB solutions. The tested solutions were stirred at room temperature for the optimum periods which previously determined (100 minutes in case of rice straw and 15 minutes in case of Egg shell powder). Samples were filtered and the dye residues in each sample were determined with UV-VIS Spectrophotometer. The removal efficiency of each adsorbent substance at different tested contact periods was investigated.

Adsorption isotherm:

Isotherm data were analyzed using Langmuir and Freundlich adsorption equations. The two equations contain two adjustable parameters and different constants were generated (Zubair and AbdelKhader, 2007 and Khan *et al.*, 2005) The Langmuir and Freundlich parameters were determined and correlation coefficients were calculated.

Langmuir model is the simplest theoretical model for monolayer adsorption onto a surface with finite number of identical sites (Agyei *et al.*, 2000 and Bajpai *et al.*, 2000. The equation is applicable to homogeneous adsorption where adsorption process has equal activation energy, based on the following basic assumptions (Abdullah *et al.*, 2009): 1. Molecules are adsorbed at a fixed number of well-defined localized sites, 2. Each site can hold one adsorbate molecule, 3. All sites are energetically equivalent, 4. There is no interaction between molecules adsorbed on neighboring sites.

The Langmuir isotherm in linear form is given as:

1/X =1/Xm . Kl + 1/C + 1/ Xm

Where:

X = is the amount of the investigated dye adsorbed per gram of the adsorbent.

C = is the equilibrium concentration.

Xm = is a constant which is refer to the monolayer capacity.

Kl = is a constant which is a measure of adsorption binding energy.

Freundlich expression is an empirical equation applicable to non-ideal sorption on heterogeneous surface as well as multilayer sorption. (Selim and Abdel-Khalek, 2010).

The linear form of Freundlich isotherm is:

Log x = Log K + 1/n Log C

Where:

K = is a constant which is a measure of adsorptive capacity.

1/n = is a constant refer to adsorption intensity. (Uddin, 2007; Khan, 2005). All the constants are specific to test conditions and the adsorbent type. (Uddin, 2007).

The plots of 1/x versus 1/C and Log X versus Log C were made to test the Langmuir and Freundlich adsorption models respectively. In each case related respective constants were determined.

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Removal efficiency%:

Removal efficiency percentage of different investigated adsorbents at different contact periods as well as with different initial dye concentrations had been calculated according to the following equation:

Removal efficiency % = (Ci - Cf/Ci) *100 where:

Ci = initial dye concentration

Cf = dye residue in the solution after treatment.

Statistical analysis:

Comparison of treatment means (all experiments were conducted in three replicates) using one-way analysis of variance (ANOVA) followed by Duncan's Multiple Range Test (DMRT) was performed to compare the different treatment means at 5% level of significance. The software SPSS, version 10 (SPSS, Richmond, USA) was used as described by Dytham (1999).

RESULTS AND DISCUSSIONS

Obtained results indicated that the two investigated adsorbents (RS and ESP) were potentially considered for inorganic pollutants (methylene blue dye) removal from their aqueous solutions. This effectiveness could be attributed to their chemical composition. Mohamed *et al.* (2016) reported that the native rice straw contained about 41.15% cellulose, 20.46% hemicellulose, and 3.91% lignin. William and Owen (1995) reported that egg shell considered an attractive material to serve as an adsorbent agent, because its chemical composition (94% calcium carbonate, 1% magnesium carbonate, 1% calcium phosphate and 4% organic material), as well as the porous nature of egg shell structure (7000-17000 pores).

The effect of Contacting period:

As shown in Table 1, MB residues decreased rapidly in the investigated solution within the first 2 minutes; and then decreased gradually with the increase of the contacting period with 1 g of each of the investigated adsorbent materials per 1 liter of the solution; until 100 minutes in case of RS and 15

minutes in case of ESP. Figures 1 and 2 revealing that the maximum removal efficiency of MB by using RS or ESP are 96.91 and 97.12 %, respectively.

Dargo *et al.* (2014) indicated that MB dye adsorbed on modified rice husk rapidly at the initial stages of the adsorption and equilibrium is attained within about 120 min. They reported that after the rapid uptake, the capacity of the adsorbent became exhausted and the adsorption would be replaced by the transportation of dye from the external sites to the internal sites of the adsorbent particles. Similar results were reported by many authors (Nwabanne and Mordi, 2009 and Singh *et al.* 2003).

Ngadi *et al.* (2013) reported that methylene blue dye was removed rapidly in 5 minutes after mixing with egg shell powder; they found that the quantity of adsorbed dye molecules rose with time and started to attain an almost constant value around 30 minutes.

Contract married (minute)	MB residues Mg/l			
Contact period (minute)	Rice straw	Egg shell		
0	100±0 ^a	100±0 ^a		
2	10.98±0.032 ^b	7.127±0.045 ^b		
5	9.59±0.214 °	5.916±0.016 ^{cd}		
10	8.52±0.185 ^d	$4.096 \pm 0.374^{\text{ f}}$		
15	7.76±0.003 ^e	2.878±0.042 ^g		
20	$6.64 \pm 0.016^{\text{ f}}$	6.69±0.173 ^{bc}		
40	5.92±0.184 ^g	4.777±0.211 ^{ef}		
60	5.76±0.297 ^g 6.655±0.288 ^{bc}			
80	4.41±0.068 ^h 6.954±0.322 ^b			
100	3.09±0.052 ⁱ	5.597±0.139 ^{de}		
120	3.99±0.087 ^h	6.435±0.622 bcd		

Table 1. Means \pm SE of MB residues at different contact periods with differentinvestigated adsorbent materials.

Means followed by different letters in each column are significantly different (Duncan's Multiple Range Test P<0.05).

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Fig 1. Removal efficiency of 1 g RS/l toward 100 mg MB/l at different contact periods.



Fig 2. Removal efficiency of 1 g ESP/l toward 100 mg MB/l at different contact periods.

The effect of adsorbents concentration:

As shown in Table 2, minimum MB residues were obtained when the experimental solution had been mixed with 1.5 and 1 g/l of rice straw or ESP, respectively. The maximum removal efficiencies of RS and ESP toward MB at different adsorbents doses were 98.57 and 97.12 %, respectively, as illustrated in Figures 3 and 4. Ngadi et al. (2013) mentioned that the adsorption efficiency increased with adsorbent concentration because there were plenty of surface area and more adsorption sites available to interact with the dye molecules provided by the increased adsorbent dosage. In contrast, the low adsorption capability might due to the saturation of adsorption sites and hence cannot further adsorb the dye molecules. Dargo et al. (2014) found that the maximum removal percentage of methylene blue was obtained when the experimental solution was mixed with 1 g/l of modified rice husk. Several investigations demonstrated that although, increasing of adsorbent dosage leads to increase of active sites for adsorption, but this phenomenon may not lead to high adsorption capacity and adsorption efficiency of adsorbent due to the over load of the adsorbent area is decreased (Verma and Mishra, 2010 and Alopes et al., 2004).

Adsorbent dose (g/l)	MB residues Mg/l				
	Rice straw	Egg shell			
0.2	14.263±1.451 ^a	9.539±0.551 ^a			
0.4	7.93±0.949 ^b	7.836±0.187 ^b			
0.6	$4.404 \pm 0.149^{\circ}$	6.418±0.016 ^c			
0.8	3.96±0.079 ^c	4.926±0.179 ^d			
1	2.454 ± 0.019^{cd}	2.878±0.042 ^e			
1.5	1.432 ± 0.048^{d}	4.165±0.318 ^d			

Table 2. Means \pm SE of MB residues in the experimental solution as treated with
different investigated adsorbent materials.

Means followed by different letters in each column are significantly different (Duncan's Multiple Range Test P<0.05).



Fig 3. removal efficiency of different doses of RS toward 100 mg MB/l.



Fig 4. removal efficiency of different doses of ESP toward 100 mg MB/l.

The effect of initial dye concentration:

Table 3 revealing that MB residues in the experimental solution as treated with either RS or ESP were affected with the initial dye concentration. When the experimental solution mixed with rice straw, MB residues directly proportionated with its initial concentration. When different initial MB experimental solutions were mixed with 1g Egg shell powder/l, the investigated dye residues slightly fluctuated until in case of 5 g/l initial MB concentration, were its residue was 3.105 mg/l, which increase sharply to 10.247 mg/l when the investigated adsorbent ESP was mixed with 100 mg MB/l experimental solution, based upon, there was no need to increase the initial MB concentration than 100 mg/l. Figure 5 showing that the highest removal efficiencies had been obtained after mixing 100, 150 and 200 mg MB/l with 1g RS/l. These values were 98.51, 98.77 and 98.9 %, respectively. However, the highest removal efficiency obtained as a result of treating the experimental solution with ESP was 94.07% at an initial dye concentration of 40 mg/l. Similar results obtained by Dargo et al. (2014) who found that the uptake of MB was rapid at lower concentration (10-15 mg/L) and as concentration increase the amount of MB adsorbed was decreased. In contrast Santhi and Manonmani, (2012) revealed that the amount of MB adsorbed per unit mass of adsorbent increased with increasing dye concentration.

Initial dye concentration (mg/l) —	MB residues (Mg/l)			
	Rice straw	Egg shell		
5	0.645 ± 0.045 g	1.724 ± 0.019 °		
10	0.757 ± 0.03 fg	1.518 ± 0.2 ^c		
20	0.807 ± 0.048 ^{ef}	2.588 ± 0.068 bc		
30	0.952 ± 0.014 ^e	1.855 ± 0.417 °		
40	1.181 ± 0.018 ^d	$2.374 \pm 0.093 \ ^{bc}$		
50	1.214 ± 0.011 ^d	3.105 ± 0.285 ^b		
100	$1.494 \pm 0.048 \ ^{\rm c}$	$10.247 \pm 0.746 \ ^{\rm a}$		
150	1.844 ± 0.002 ^b	_		
200	2.206 ± 0.124 ^a	_		

Table 3. Means \pm SE of MB residues in the experimental solution as affectedwith initial dye concentrations.

Means followed by different letters in each column are significantly different (Duncan's Multiple Range Test P<0.05).



Fig. 5. Removal efficiency of 1 g RS/l as mixed with different initial MB concentrations.



Fig. 6. Removal efficiency of 1 g ESP/l as mixed with different initial MB concentrations.

The adsorption isotherms:

The adsorption isotherms data, as shown in Table 4 for RS and in Table 5 for ESP were fitted to both the Langmuir and Freundlich isotherm equations. The typical graphical representations of the linearized plots are shown in figures 7 and 8 for adsorption of MB on RS and ESP, respectively, according to Langmuir equation; as well as in Figures 9 and 10 for adsorption of MB on RS and ESP, respectively, according to Freundlich equation. The results show that the adsorption process could be described well with both Langmuir and Freundlich isotherms. The experimental equilibrium data fitted well to both equations with correlation coefficient values greater than 0.9 for RS while these values are 0.9686 and 0.9811 for Langmuir and Freundlich equations, respectively, while these values for ESP are 0.8268 and 0.9601, respectively. Similar results were reported in a related work (Okeola and Odebunmi, 2010).

RS dose (g/l)	0.2	0.4	0.6	0.8	1	1.5
C (Dye conc. mg/l)	14.26	7.93	4.4	3.96	2.45	1.43
Dye removed (mg/l)	85.74	92.07	95.6	96.04	97.55	98.57
X (dye removed/g of adsorbent (mg/g)	428.7	230.18	159.33	120.05	97.55	65.71
1/C	0.07	0.126	0.227	0.253	0.408	0.699
1/X	0.0023	0.0044	0.0063	0.0083	0.0103	0.015
Log C	1.154	0.899	0.644	0.5977	0.3899	0.156
Log X	2.632	2.362	2.202	2.079	1.989	1.818
Langmuir data -	1/xmk	0.0198				
	1/xm	0.0019				
Langmuir constants	Xm	526.316				
	K	0.096				
	\mathbf{R}^2	0.9686				
Freundlich data -	1/n	0.8045				
	log k	1.6654				
Freundlich constants	n	1.24				
	K	46.28				
	R^2	0.9811				

Table 4. Isothermal data for RS as an Adsorbent.

ESP dose (g/l)	0.2	0.4	0.6	0.8	1	1.5
C (Dye conc. mg/l)	9.54	7.84	6.42	4.93	2.88	4.165
Dye removed (mg/l)	90.46	92.16	93.58	95.07	97.12	95.84
X (dye removed/g of adsorbent (mg/g)	452.3	230.4	155.97	118.84	97.12	63.89
1/C	0.105	0.128	0.156	0.203	0.347	0.24
1/X	0.0022	0.0043	0.006	0.0084	0.010	0.0157
Log C	0.98	0.894	0.807	0.692	0.459	0.62
Log X	2.655	2.363	2.193	2.075	1.987	1.805
Langmuir data –	1/xmk	0.0302	_			
	1/xm	0.0007	_			
Langmuir constants	Xm	1428.57	_			
	K	0.023	_			
	\mathbb{R}^2	0.8268	-			
Freundlich data –	1/n	2.131	-			
	log k	0.5165	-			
Freundlich constants	n	0.469	-			
	K	3.285	_			
	\mathbb{R}^2	0.9601	-			

 Table 5. Isothermal data for ESP as an Adsorbent.



- **Fig 7.** Application of Langmuir equation to the experimental data points Determined for the adsorption of MB on the RS. The straight line represents a linear regression fit to the result, Where:
 - X = is the mass of MB per unit mass of RS.
 - C = is the concentration after adsorption.
 - R = is the regression co-efficient.



Fig 8. Application of Langmuir equation to the experimental data points determined for the adsorption of MB on the ESP. The straight line represents a linear regression fit to the result.



Fig 9. Application of Freundlich equation to the experimental data points determined for the adsorption of MB on the RS. Sorption of MB on the ESP. The straight line represents.



Fig.10. Application of Freundlich equation to the experimental data points determined for the adsorption of MB on the ESP.

The Langmuir and Freundlich constants determined from the slopes and intercepts of the respective plot are summarized in tables 4 and 5. Although the constants are specific to test conditions and adsorption type, the obtained results indicate comparable assessment of the investigated adsorbents. The constant X m in the Langmuir isotherm which represents a practical limiting adsorption capacity is useful in comparing performance adsorption of different adsorbents. The value of X m relates directly with MB adsorbed from solution, this value for ESP is higher than that of RS, while the Freundlich constant n of RS is higher than that of ESP.

CONCLUSION

The two investigated adsorbents, rice straw and egg shell powder were found potentially effective for removing the basic dye, Methylene blue, as an organic pollutant, from its aqueous solutions. It is recommended to use such low cost materials for improving the quality of the huge amounts of water, which available in low quality, resulting in these types of waters became more suitable for different purposes.

REFERENCES

- Abdullah, M.A.; L. Chiang and M. Nadeem, 2009. Comparative evaluation of adsorption kinetics and isotherms of a natural product removal by Amberlite polymeric adsorbents, Chemical Engineering Journal, 146: (370–376).
- Agyei, N. M.; C.A. Strydom and J.H. Potgieter, 2000. An Investigation of Phosphate Ion Adsorption from Aqueous Solution by Fly Ash and Slag, Cem. Concr. Res., 30: 823–826.
- Arunlertaree, C; W. Kaewsomboon; A. Kumsopa; P. Pokethitiyook and P. Panyawathanakit, 2007. Removal of lead from battery manufacturing wastewater by egg shell. Songklanakarin J. Sci. Technol., 29 (3): 857-868.
- Bajpai, A. K.; M. Rajpoot and D.D. Mishra, 2000. Static and Kinetic Studies on the Adsorption Behavior of Sulfadiazene," Adsorption, 6: 349–357.
- Berneth, H., 2003. Cationic dyes. In Ullamnn's Encyclopedia of Industrial Chemistry. 6th Ed., Wiley-VCH, Weinheim, Germany, (6): 585-591.
- Dargo, H.; N. Gabbiye and A. Ayalew. 2014. Removal of Methylene Blue Dye from Textile Wastewater using Activated Carbon Prepared from Rice Husk. International J. of Innovation and Scientific Research, 9 (2): 317-325.
- Dogan, M.; M. Alkan; A. Turkyilmaz and Y. Ozdemir, 2004. Kinetics and mechanisms of removal of methylene blue by adsorption on perlite. J. of Hazardous Materils, volume 109 (1-3): 141-148.
- Dytham, C., 1999. Choosing and Using Statistics: A Biologist's Guide. Blackwell Science Ltd., London, UK, 147 pp.
- Egyptian Environmental Affairs Agency (EEAA), 2008, and Ministry State for Environmental Affairs, Rice Straw Utilization Program Report.

- El-Gammal, M.I. and A.A. Shakour. 2001. Emission of pollutants from harvest and burning of rice straw in Egypt villages (North East of Nile Delta)," Journal of Union of Arab Biologists Cairo A Zoology, 15: 191– 206.
- El-Sherbiny, M.F.; M.A. Hanna; A.A. Al-Sarawy and M.A. Farid, 2009. Removal of Some New Direct Sulpho Aryl Azo Dyes from Aqueous Solutions by Adsorption onto Different Types of Carbon. Mansoura engineering journal, (32): 1-20.
- Fan, J.; Y.G.J. Wang and M. Fan, 2009. Rapid decolorization of azo dye methyl orange in aqueous solution by nanoscale zerovalent iron particles, J. Hazard. Mater., 166: 904.
- Food and Agriculture Organization of United the Nations (FAO), 2006. Record Rice Yields for Egypt.
- Fu, Y. and T. Viraraghavan, 2001. Fungal decolorization of dye wastewaters: a review, Bioresour. Technol., 79: 251.
- Garg, V.K.; R. Gupta; A.B. Yadav and R. Kumar, 2003. Dye removal from aqueous solution by adsorption on treated qawdust, Bioresource Technology, 89: 121-124.
- Goel, K.A.; A.K. Awasthi and S. K. Tyagi, 1981. Haematoenzymology of Heteropneustes under chem'coazo stress of bismark brown. Curr. Sci., 50 (19): 875-876.
- Kannan, N. and M.M. Sundaram, 2001. Kinetics and mechanism of removal of methylene blue by adsorption on various carbons, a comparative study, Dyes and Pigments, 51: 25-40.
- Kapdan, I.K.; F. Kargi; G. Mcmullan and R. Marchant, 2000. Environmental Technology, 21: 231-236.

- Karanjkar, D.M.; D.V. Muley and S.A. Manjare, 2000. Acute toxicity of industrial effluents to Labeo rohita. Proc. Acad. Environ. Biol., 9 (Suppl.), 30.
- Keshtkar, H. and L.L. Ashbaugh, 2007. Size distribution of polycyclic aromatic hydrocarbon particulate emission factors from agricultural burning," Atmospheric Environment, 41 (13): 2729–2739.
- Khan, A.R.; H. Tahir; F. Uddin and H. Uzma, 2005. "Adsorption of methylene blue from aqueous solution on the surface of wool fiber and cotton fiber." J .of Applied Science and env. Manag., 9 (2): 29-35.
- Kuh, S.E. and D.S. Kim, 2000. Removal characteristics of cadmium ion by waste egg shell. Environ. Technol., 21: 883-890.
- Lopes, A; S. Martins; A. Morao; M. Magrinho and I. Gonçalves, 2004. Degradation of textile dye C.I.Direct Red 80 by Electro chemical process", Portugaliea Electrochemical Acta, 279-294.
- Mohamed, S. R.; T. A. El-Desouky; A. M. Hussein; S. S. Mohamed and Kh.M. Naguib. 2016. Modified rice straw as adsorbent material to remove Aflatoxin B1 from Aqueous media and as a fiber source in Fino bread.J. of Toxic. Volume 2016, 10 pages.
- Murugesan, A.G.; Sm. P. Muthu and M.A. Haniffa, 1989. Cytopathological changes in erythrocytes of the catfish Heteropneustes fossilis (Bloch) exposed to textile-mill effluent. Curr. Sci., 58 (5): 268-270.
- Ngadi, N.A; C.C. Ee and N.A. Yusoff, 2013. Removal of Methylene Blue Dye by Using Eggshell Powder. Jurnal Teknologi (Sciences & Engineering) 65 (1): 63–71.
- Nwabanne, J.T. and M.I. Mordi, 2009. Equilibrium uptake and sorption dynamics for the removal of a basic dye using bamboo. African Journal of Biotechnology, 8 (8): 1555-1559.

- Okeola, F.O. and E.O. Odebunmi, 2010. Freundlich and Langmuir Isotherms Parameters for Adsorption of Methylene Blue by Activated Carbon Derived from Agro-wastes. Advances in Natural and Applied Sciences, 4 (3): 281-288.
- O'Mahony, T.; E. Guibal and J.M. Tobin, 2002. Enzyme and Microbiology Technology, 31: 456.
- Özer, A. and G. Dursun, 2007. Removal of Methylene Blue from Aqueous Solution by Dehydrated Wheat Bran Carbon", J. of Hazardous Materials, 146: 262-269.
- Parr, J.F.; R.I. Papendick; S.B. Hornick and R.E. Meyer, 1992. Soil quality: attributes and relationship to alternative and sustainable agriculture. American Journal of Alternative Agriculture, 7: 5–11.
- Porter, J.F.; G. McKay and K.H. Choy, 1999. The prediction of sorption from a binary mixture of acidic dyes using single-and mixed-isotherm variants of the ideal adsorbed solute theory. Chemical Engineering Science, 54 (24): 5863-5885.
- Rana, K.S. and S. Raizada, 1999. Acute toxicity of tannery and textile dye effluents on a common teleost, Labeo rohita: Histological alterations in liver. J. Environ. Biol., 20(1): 33-36.
- Santhi, T. and S. Manonmani, 2012. Adsorption of methylene blue from aqueous solution onto a waste aquacultural shell powders (prawn waste). Sustain. Environ. Res., 22 (1): 45-51.
- Selim, K.A. and N.A. Abdel-Khalek, 2010. Comparative evaluation of adsorption isotherms of polyacrylic acid onto calcium carbonate. The Journal of ore dressing, 12 (24): 35-41.
- Selvam, K.; K. Swaminathan and K.S. Chae, 2003. Bioresource Technology., 88: 115-119.

- Shahabuddin, A.M.; M.T. Oo.; Y.Yi; D.P. Thakur; A.N. Bart and J.S. Diana, 2012. Study about the effect of rice straw mat on water quality parameters, plankton production and mitigation of clay turbidity in earthen fish ponds. World J. of Fish and Marine Sci., 4 (6): 577-585.
- Singh, K.P.; D. Mohan; S. Sinha; G.S. Tondon and D. Gosh, 2003. Color Removal from Wastewater Using Low-Cost Activated Carbon Derived from Agricultural Waste Material", Ind. Eng. Chem. Res., (42): 1965-1976.
- Stadelman, W.J., 2000. Eggs and egg products. In F.J. Francis (ed). Encyclopedia of Food Science and Technology. 2nd ed. John Wiley & Sons. New York., 593-599.
- Tacon, A.G.J. and I.P. Forster, 2003. Aquafeeds and the environment: Policy implications. Aquaculture, 226 (1-4): 181-189.
- Uddin, M. T.; M.S. Islam and M.Z. Abedin, 2007. Adsorption of phenol from aqueous solution by water hyacinth ash." ARPN J of Engineering and Applied sciences, 2(2): 121-128.
- Verma, V.K. and A.K. Mishra, 2010. Kinetic and isotherm modeling of adsorption of dyes onto rice husk carbon. Global Nest Journal, 12 (2): 190-196.
- William, J.S. and J.C. Owen, 1995. Egg science and technology. 4th ed. Food Product Press. New York., 590p.
- Zollinger, H., 1991. Color chemistry: synthesis, properties and applications of organic dyes and pigments, 2nd Ed. VCH Publisher, New York.
- Zsoy, H.D.; A. Unyayar and M.A. Mazmanci, 2005. Decolourisation of reactive textile dyes Drimarene Blue X3LR and Remazol Brilliant Blue R by Funalia trogii ATCC 200800, Biodegradation, 16: 195.
- Zubair, B. and B. AbdelKhader, 2007. Correlation with different models of adsorption isotherms of m-xylene and toluene on zeolites." J. of Applied Sciences in Environ. sanitation, 2 (2): 43-46.

إزالة صبغة أزرق الميثيلين كأحد الملوثات العضوية من المحاليل المائية باستخدام بعض المواد الطبيعية قليلة التكلفة

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الملخص العربسي

تم القيام بهذا العمل لإختبار كفاءة كل من قش الأرز كأحد النواتج الثانوية قليلة التكلفة المتخلفة عن زراعة الأرز وكذلك قشور بيض الدجاج كأحد المخلفات الطبيعية عديمة الكلفة في إزالة صبغة أزرق الميثيلين كأحد الملوثات العضوية من محلولها المائي.

إن عملية إزالة الصبغات من الوسط المائي لمن الأهمية بمكان حيث أن الصبغات نتتج من العديد من العمليات الصناعية مثل الصباغة وطباعة الورق والتصوير الفوتوغرافي الملون وكإضافات إلي المنتجات البترولية والعديد من الصناعات الأخري. وقد وجد أن المياه الناتجة عن تلك الأنشطة الصناعية تكون ملونة بصورة كبيرة وتكون مرئية حتي بالنسبة للتركيزات الصغيرة التي لا تزيد عن جزء واحد في المليون مما يغير من صفات جودة المياه ويجعلها غير ملائمة للإستخدامات المختلفة كما أنه يؤثر علي عملية البناء الضوئي في البيئة المائية حيث يقال من إختراق الضوء للمياة. كما وجد أن المحاليل المحتوية علي صبغات لها العديد من التأثيرات السلبية علي الأسماك حيث تزيد من نسب وتزداد أهمية إجراء مثل تلك البحوث في مصر لإزدياد الحاجة لإيجاد مصادر بديلة للأسماك.

وقد تم إجراء عدد من التجارب في هذه الورقة البحثية لبيان تأثير كل من فترة الخلط بين المحلول المحتوي علي الصبغة ومواد الإزالة المختبرة وكذلك تحديد التركيزات المثلي من مواد الإزالة بالإضافة لبيان تأثير تركيز الصبغة الأولي في المحلول علي نسب إزالتها.

تبين من النتائج المتحصل عليها في نهاية هذا العمل أن أفضل مدة للخلط بين محلول الصبغة وكل من قش الأرز ومسحوق قشور البيض كانت 100 و 15 دقيقة علي التوالي. بينما كانت التركيزات الأمثل لكل من قش الأرز ومسحوق قشور البيض 1,5 و 1 جرام/ لتر علي التوالي. بإختبار عدد من

التركيزات المختلفة لصبغة أزرق الميثيلين تبين أنه بزيادة تركيزات الصبغة المختبرة يقل معدل إدصاص تلك الصبغة لوحدة الوزن من مواد الإدمصاص المختبرة.

تم تطبيق نتائج الإدمصاص المتحصل عليها على النموذجين الرياضيين المتعارف عليهما لانجماير وفرندليش وتم حساب الثوابت الدالة على طاقة وكفائة الإدمصاص وكذلك تم حساب معامل الإرتباط لكل من مادتي الإدمصاص المختبرتين مع النموذجين المطبقين، حيث تبيين ملائمة النموذجان للتطبيق علي كل من قش الأرز ومسحوق قشور البيض. كانت أفضل نسب إزالة لصبغة أزرق الميثيلين من محلولها المائي بعد خلطه بكل من قش الأرز أو مسحوق قشور البيض هي 98,9 و 97,12 % علي التوالي.

نستطيع أن نخلص من هذا العمل إلي كفاءة كل من قش الأرز وقشور البيض كمواد طبيعية قليلة التكلفة في إزالة نسب كبيرة جدا من صبغة أزرق الميثيلين من مياه الصرف الأمر الذي يؤدي لتحسين خواص جودة المياه لتصبح أكثر ملائمة للعديد من الإستخدامات المختلفة.