ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

Removal of single and binary some organic dyes from aqueous solution by waste eggs paper packing dishes

A.A. Emam, A. A. El-Bayaa, N.A. Badawy , A.M.Hussien
Chemistry Department, Faculty of Science, Al-Azhar University (Girls), Nasr City, Cairo, Egypt

Manuscript Info

Manuscript History:

Received: 14 May 2015
Final Accepted: 19 June 2015
Published Online: July 2015

Key words:

Waste eggs paper packing dishes, Basic dye , Reactive dye and Adsorption

Corresponding Author

A.M.Hussien

Abstract

Adsorption is one of the most promising decolorization techniques in dyeing wastewater treatment. Adsorption techniques for wastewater treatment have become more popular in recent years owing to their efficiency in the removal of pollutants too stable for biological methods. The main advantage of adsorption recently became the use of low-cost materials, which reduces the procedure cost. Waste eggs paper packing dishes (WEP) and a new sorbent based on (WEP) was developed for the removal of reactive brilliant blue (RB5) and suffranin O (BR2) in single and binary systems from aqueous solutions. SEM and IR were used to analyze the morphology and chemical groups of the (WEP) and (TWEP).before and after dye sorption.

INTRODUCTION

Polluted water was cause of various diseases that can seriously affect public health. Toxic substances contained in polluted water can be stored in grown plants whose the consumption later can cause digestive diseases, liver and kidney damage. Marine pollution is the source of the degradation of the aquatic flora and fauna. The harmful substances in the wastes that flow directly into the seas are more or less absorbed by marine organisms. Many plant and animal species are already extinct and while others are endangered **[Zamouche and Hamdaoui, 2012].** The use of synthetic chemical dyes in various industrial processes has increased considerably **[Madrakian *et al.*, 2012].** Chemicals used for the synthesis of dyes are also hazardous to human life **[Tahir *et al.*, 2009].** Some areas where these chemicals are frequently used are paper and pulp manufacturing, plastics, dying of cloth, leather treatment, printing **[Madrakian *et al.*, 2012],** cosmetics **[Sulak *et al.*, 2007],** food technology, hair colorings **[Akar *et al.*, 2013],** petroleum, paint, drugs for photodynamic therapy against cancer **[Tahir *et al.*, 2009],** biomedical laboratories **[Zamouche and Hamdaoui, 2012],** guest-host liquid crystal displays, solar cells, mineral processing industries and etc. **[Hou *et al.*, 2011].** There are more than 100,000 dyes available commercially, most of which are difficult to biodegrade due to their complex aromatic molecular structure and synthetic origin **[ÇiÇek *et al.*, 2007].** Color is the first contaminant to be recognized in water and has to be removed from wastewater before discharging it into water bodies **[Peng *et al.*, 2012].** Colored water can affect plant life; it inhibits the growth of biota and also has a tendency to chelate metal ions which result in micro-toxicity to fish and other organisms **[Peng *et al.*, 2012].** For these reasons, the treatment of dye-effluents is essential prior to their discharge into the receiving water bodies is of significant importance from an environmental and economic point of view and there are many methods for wastewater treatment **[Madrakian *et al.*, 2012**]. Various physicochemical and biological techniques can be employed to remove dyes from wastewaters. They include the membrane filtration coagulation/ flocculation, **[Zhong *et al.*, 2011, Mohan *et al.*, 2002 and Acuner *et al.*, 2004**], adsorption, ion exchange, advanced oxidation (chlorination, ozonation), flotation, chemical reduction and biological treatment (bacterial and fungal biosorption, photocatalytic degradation [**Sun *et al.*, 2008]**, biodegradation **[Azmi *et al.*, 1998]**, solar photo-Fenton degradation

[Durán *et al.*, 2008], electrochemical degradation [**Fan *et al.*, 2008].** Basic dyes are known as cationic dyes. This a class of synthetic dyes, that act as bases and when made soluble in water, they form a colored cationic salt, which can react with the anionic sites on the surface of the substrate. The basic dyes are the brightest class of soluble dyes used by the textile industry, but their doctorial value is very high **[Zamouche and Hamdaoui, 2012].** Reactive dyes can be used to dye wool and nylon, in the latter case they are applied under weakly acidic conditions. The most important characteristic of reactive dyes is the formation of covalent bonds with the substrate to be coloured, i.e. the dye forms a chemical bond with cellulose, which is the main component of cotton fibers. Unlike other dyes, it actually forms a covalent bond with the cellulose or protein molecule. Once the bond is formed, what you have is one molecule, as the dye molecule has become an actual part of the cellulose fiber molecule. The reactive dyes, which represent the largest class of dyes used in textile processing industries, are almost azo compounds, i.e. molecules with one or several azo (N=N) bridges linking substituted aromatic structures. These dyes are designed to be chemically and photolytically stable; they exhibit a high resistance to microbial degradation and are highly persistent in natural environment. The release of these compounds into the environment is undesirable, not only for aesthetic reasons, but also because many azo dyes and their breakdown products are toxic and/or mutagenic for life.

Paper is an important part of our everyday life and also one of the various cellulosic biomass wastes generated in voluminous amounts in various fields. It is not a surprise that paper can be recycled and reused as paper only for a limited number of times due to the shortening of fibre length and lowering of the fibre tensile strength at each successive step of recycling. As a result, it loses most of its value and becomes worthless garbage which occupies 30–40% of landfill sites in developed countries. Also, the fibres left over from the process of paper production, which contain over 70% of pure cellulose, have been usually discarded with the wastewater in amounts of several thousand tonnes a year, thus presenting a significant environmental pollution problem. Consequently, from the perspectives of both environment and economy, efforts are being made to reclaim value from this cheap biomass in the form of energy and advanced functional materials by the effective use of its unique characteristics **[Nikolov *et al.*, 2000]**,. Waste eggs paper packing dishes materials (WEP) as sorbent have little or no economic value and often pose a disposal problem. A new sorbent based on (WEP) was developed via chemical modification in which quaternary ammonium cationic groups were introduced into the cellulose backbone of (TWEP). The aim of the present work is to explore the possibility of utilizing (WEP) and (TWEP) as a sorbent for the removal of single and binary suffranin O (C.I. basic red 2) and reactive brilliant Blue K-Rl (C.I. Reactive blue 5) from aqueous solution.

2. Material and Methods

All the chemicals used throughout this study were of analytical-grade reagents and the adsorption experiments were carried out at room temperature (25 ± 2 °C)

2.1 Adsorbent

2.1.1. Waste eggs paper packing dishes (WEP)

The waste eggs paper packing dishes materials (WEP) were torn up into small pieces ($1cm^2$) and immersed in bidistilled water for 72 hours under constant stirring with water changes every 12 hours. Waste papers were dried for 5 days in sunlight. Dried Waste papers were grounded in a domestic mixer grinder. After grinding, the powders were again washed and dried. Different sized adsorbent were stored in plastic container for further use.

2.1.2 Treated waste eggs paper packing dishes (TWEP)

A 20 gm sample of waste eggs paper packing dishes powder and 500 ml of 10% NaOH were added into three necks round bottom flask and agitated for 1h at room temperature. then half of the solution was removed and immediately 100 ml of distilled water and 160 ml epoxy chloropropan were added .The mixture was heated in 65^0C water bath and stirred for 6 h .the solution was removed from heat and 220 ml of 34% triethyle amine solution was added .The mixture was heated in 80^0 C water bath and agitated for 3 h .The product was washed with ethanol and distilled water. The solution pH was then adjusted around 7 using 0.1M NaOH and 0.1M HCl. Finally, the product was cleaned with distilled water until the pH was around 7. The treated waste eggs paper packing dishes (TWEP) were dried at 60c for 12 h. The dried (TWEP) was grounded in a domestic mixer grinder. After grinding, the powders were again washed and dried. Different sized adsorbent were stored in plastic container for further use.

2.1.3. Determination of the point of zero charge

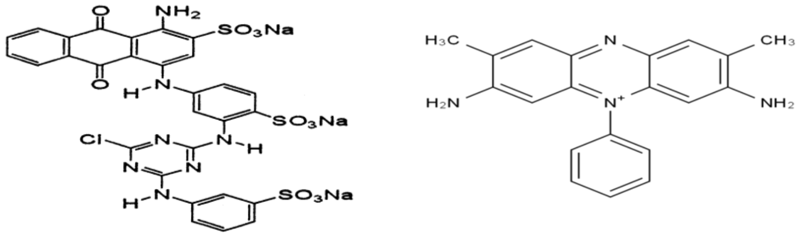
The point zero charge (pH_{pzc}) of adsorbent was determined by the solid addition method. The net charge of surface is zero on the adsorbent surface at pH_{pzc}, therefore, no activation of acidic or basic functional groups are detected on the solution pH. Batch equilibrium method was used for the determination of point of zero charge. To each of the flask 0.1 g of adsorbent was added including 100 ml solution KNO_3 (0.01 N) in the pH range between 2.0 to 10.0.

The initial pH of solutions were adjusted by adding drops of (0.5 N) NaOH and (0.5 N) HCl solutions and each flask was sealed and shaken thoroughly for 48 h at room temperature and the final pH of the solution was measured and recorded. The total charge adsorbed on waste eggs packing dishes surface was determined by ΔpH (the difference in the value of pH of the solution before and after 48 h). The intersection of obtained curve with pH_0 axis indicated the pH_{pzc} value (Farahani et al., 2011).

2.2. Adsorbate

2.2.1. Chemical dye structure

The following dyestuffs under investigation are a cationic dye suffranin O obtained from El-Gomhoria Company , Egypt having molecular formula $C_{20}H_{19}N_4Cl$ (mol wt. 350.85 and Reactive brilliant Blue K-Rl (C.I. Reactive blue 5) obtained El-Gomhoria Company , Egypt having molecular formula $C_{29}H_{17}ClN_7Na_3O_{11}S_3$ (mol wt. 840.11) scheme (1).



Scheme (1) a-Chemical structure of (RB5) **b- Chemical structure of (BR2)**

2.2.2. Dye Solutions

A stock dyes solution was prepared by dissolving 1 g in 1000 ml bidistilled water. These solutions were kept in the dark bottle stopper very well. Other concentrations were prepared from stock solution by dilution.

2.3. Batch Adsorption Studies

A known weight of adsorbent was shaken together with 40 ml of an aqueous C.I. reactive blue 5 and C.I. basic red 2 dye solutions in a 50 ml stopper bottle maintained at 25^0C for about 24 h. The initial concentration of dyes was about (15 ppm) in all experiments, except for that carried out to examine the effect by the initial concentration of dye. Adsorption experiments were conducted in batch mode to evaluate the effects of various parameters, such as pH, initial dye concentrations, and adsorbent doses, on the adsorption of C.I. reactive blue 5 and C.I. basic red 2.

2.3.1 Effect of dose

The sorption of dyes on (WEP) and (TWEP) were studied by changing the amount of sorbent in aqueous solution while the initial dye concentration are (15ppm) C.I. basic red 2 and C.I. reactive blue 5 respectively. The other variables were kept constant**.** The amount of dyes adsorbed was obtained by contacting 40 ml of dye solutions with different amount of adsorbent ranging from (0.25 to 3.5g/l) . The mixture was leaved until equilibrium time (24h **)** and then, a sample was taken for analysis.

2.3.2 Comparative study of dye adsorption by (TWEP) and (WEP)

In this study the dye adsorption capacities of (TWEP) and (WEP) for BR2 and RB5 were compared in binary dye solution 0.6 g of each sorbent was agitated in 40 ml of (15 ppm) binary dye solution for 24 h.

2.4. Determination of absorption maxima (λ_{max}) of dyes

The absorption maximum was determined by using a spectrophotometer. Optical density of dye solution in water was observed at different wavelength between visible regions (340-700nm). The wavelength where, the dye showed maximum absorbance is taken as absorption maximum of the dye; λ_{max} = 675 nm for C.I. reactive blue 5 and λ_{max} = 523 nm for C.I. basic red 2 were observed.

The amount of adsorption was calculated based on the difference of the dye concentrations in the aqueous solutions before and after adsorption. The absorbance of dyes in aqueous solutions was measured with UV/ visible spectrophotometer at wavelength corresponding to the maximum absorbance. Before each measurement, the baseline of the spectrophotometer was calibrated against the solvent. The concentration of dye in the aqueous solutions before and after adsorption was obtained using the standard curve. These data were used to calculate the adsorption capacity, of the adsorbent. Then, a diagram of adsorption capacity, against equilibrium concentration, was plotted. The amount adsorbed of dye q_e and the percentage sorption, were calculated using the following relationships [**Kannan and Sundaram (2001]**

$$q_e = (C_0 - C_e)V/ W \qquad (1)$$

$$\text{Sorption \%} = 100\,(C_0 - C_e)/ C_0 \qquad (2)$$

where q_e the amount of adsorption at equilibrium, (mol/g) , C_0 and C_e (moll^{-1}) are the initial dye concentration and the dye concentration at equilibrium, respectively; V is the volume of the dye solution; and W is the weight of adsorbent.

2.5. Apparatus

The spectrophotometric measurements were carried out on V-530 UV-VIS spectrophotometer (made in Japan) .Scanning electron microscopy (SEM) analysis (made in Japan) was carried out on the (WEP) and (TWEP), to study its surface texture before and after dye adsorption. Fourier Transform Infrared(FT.IR) Spectrometer Model Type Mattson- Infinity Series Bench top 961 analysis was applied on the (WEP) and (TWEP) and dye adsorbed (WEP) and (TWEP) to determine the surface functional groups, where the spectra were recorded from 4000 to 400 cm^{-1}.

3. Results and Discussion

3.1 Determination of the point of zero charge of (WEP)

It is well known that aqueous phase distribution of solute species is dependent on the pH of the solution. The data on the adsorption of solute species onto the surface of adsorbents at different pH values should give a fairly good idea about the pH range favorable for the adsorption process. The point zero charge of (WEP) was determined. Since KNO_3 solution was used, it is desirable to have a fixed background electrolyte concentration that is high enough to minimize the total salt concentration changes during the titration and no clear effect of KNO_3 was found on mobility. The pH_{pzc} values were known by determining the position where the resulting curves cut through the pH_0 axis as shown in Fig. (1).The pH_{pzc} was found to be 6.8 for (WEP) sample. This is a convenient index of a surface when the latter becomes either positively charged or negatively charged as a function of pH. When the pH of the aqueous solution is below the pH_{zpc}, the surface of the adsorbent will become positively charged. Meanwhile, the surface of the adsorbent will become negatively charged when the solution pH is greater than pHzpc (Shukla *et al.*, 2002).

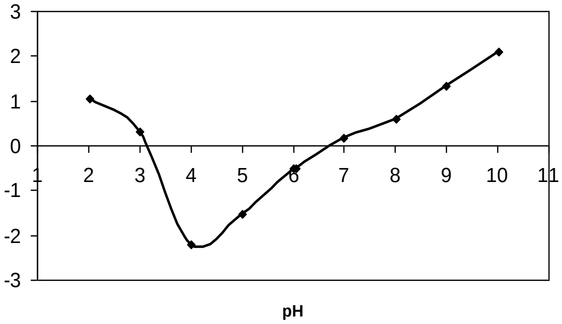
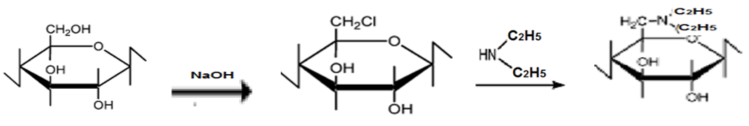


Fig.(1).The point zero charge of (WEP)

Cellulose units are being the major component of paper**.** Unlike commercially available cellulose, waste paper cellulose is highly amorphous and hence is more accessible to chemical modification. With a target chemical modification of the surface cellulose fibers based on anchoring functional groups displaying high affinity toward specific compounds, one can expect to boost the adsorption capacity toward pollutants dissolved in water. Chemical modification of (WEP) was performed according to scheme (2).



Wastepaper chlorinated paper diethyl amine type

Scheme 2 Chemical modification of (WEP) to (TWEP)

3.2. Adsorption of anionic and cationic dyes on (WEP) and (TWEP)

There are several factors on which the effectiveness of adsorption process depends upon these adsorption conditions which may either be the nature of the adsorbent (acidic/ basic) or the characteristics of adsorbent which includes the high surface area, dosage, pore size distribution, ash content and hydrophobicity. The acidity or basicity of the adsorbent depend upon the presence of hetero atoms such as oxygen, which can form phenols, ethers, lactones ketone, carboxyl and nitrogen in the form of amines and nitro groups. On the other hand, adsorption also depends on the nature of the adsorbate where it depends on its hydrophobicity, and polarity of the molecule.

3.2.1 Effect of adsorbent dosage on adsorption dye by (WEP) and (TWEP) in single dye solutions

The experiment carried by taking different adsorbent doses (0.25–3.5 g/l) in order to find the effect of different doses of (WEP) and (TWEP) on the removal of C.I. basic red 2 and C.I. Reactive blue 5. The removal efficiency of BR2 by (WEP) increased from 10.19 % to 76 %.

The removal efficiency of RB5 by (WEP) and (TWEP) increased from 1.1% to 4.92% and from 56.236 % to 92.603% respectively .When adsorbent dose was increased the number of adsorption sites or the surface area increases with the weight of adsorbent and hence results in a higher percent of dye removal at a high dose **[Panneerselvam *et al*., 2011]**. As shown in Fig. (2), the sorption equilibria of dye were reached maximum at 1.5g/l then the removal of dyes remained almost invariable above this dosage. Therefore, 1.5g/l appears to be the optimum sorbent dosage **[Wang et al.,2009].** The removal of BR2 increased with the increase in (WEP) dosage and the solution became colorless when dosage exceeded 1.5g/l

The adsorption capacity of C.I. basic red 2 and C.I. Reactive blue 5 dyes decreased with the increasing dosage of (WEP) and (TWEP*)*. The sorbents are not fully utilized because of the increase in available sorption sites with increasing adsorbent dosage. C.I. basic red 2 adsorption capacities decreased gradually from 24.503mg/g at adsorbent dosage of 0.25 g/l to with 13.053mg/g at adsorbent dosage 3.5 g/l. while C.I. Reactive blue 5 adsorption capacity decreased gradually from 134.966 mg/g to 15.875 mg/g. These results may be due to the overlapping of adsorption sites as a result of adsorbent particle overcrowding (Garg ***et al*., 2003**). Moreover, the high adsorbent dosage could impose a screening effect on the dense outer layer of the cells, thereby shielding the binding sites from metal (Pons and Fuste 1993). The plots of log Q_e vs (dose) Fig (3)are found to be linear and the value of (R≈1.0) calculated by linear regression method. This suggests that the adsorbed species/solute may either block the access to the internal pores or cause particles to aggregate and thereby resulting in the availability of active sites for adsorption **Kannan and Sundaram, (2001).**

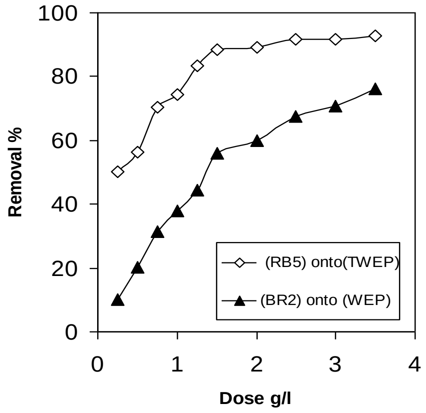


Fig.(2): Effect of (WEP) and (TWEP) doses on removal % of BR2 and RB5 dye respectively in single System at concentration 60 ppm ,time 24 hr.

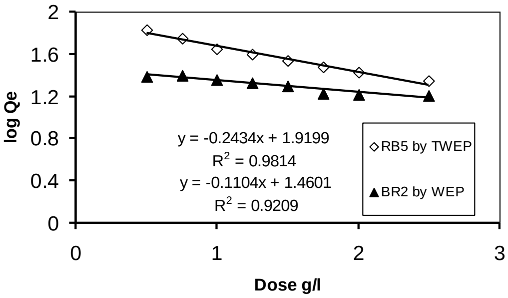


Fig.(3): The plots of log Q_e vs doses of (WEP) and (TWEP) for BR2 and RB5 dye respectively in single System at concentration 60 ppm , equilibrium time 24 hr.

3.2.2 Effect of adsorbent dosage on adsorption dye by (WEP) and (TWEP) in binary dye solutions

In binary systems BR2 + RB5 were carried out in solutions containing both dyes at initial concentrations constant in the concentration ratio 1:1.The influence of varying dose of (WEP) and (TWEP) in binary dye solutions was studied. The removal % and dye sorption capacities were investigated.

The effect of sorbent dosage on the removal of dyes is shown in Table (1). Along with the increase of sorbent dosage from 0.5 to 2.5 g/l, the percentage of dye removal increased. This is due to the increase of active sites for adsorption of dye molecules with increasing sorbent dosage. The sorption equilibria of the dyes were reached at 2.0 g/l and the removal of dyes remained almost invariable above this dosage. Therefore, it appears to be the optimum sorbent dosage. The adsorption of BR2 dye by (WEP) in binary system of RB 5+ BR2 is higher than RB5. Since the (WEP) bears a negative charge, and therefore it is the major functional group in the adsorption of BR2. On other hand, (TWEP) will inhibit the adsorption of RB5 dye.

The adsorption capacity of (WEP) and (TWEP) decrease with increase in dose for all the dye systems as shown in Table (2). As dose increased from 0.5 to 2.5 g/l ,Q_e decreased from 2.923 to 1.126 mg/g and 0.488 to 0.328mg/g when RB5 adsorbed by (TWEP) and (WEP) respectively .while Q_e of BR2 decreased from 4.965 to 1.773 mg/g and from 0.738 to 0.388mg/g when adsorbed by (WEP) and (TWEP) respectively in binary system .

The specific sorption capacities of the dye decreased with increasing adsorbent dose because at low doses, the active sites were effectively utilized. But, as the adsorbent dose was increased, a significant portion of the available active sites on the adsorbent overlapped which resulted in reduction in specific uptake. Similar observations were reported [**Mohammed AM; et al,2011**, **Hassanein FT; et al,2010 and Ponnusamy V et al,2009]**

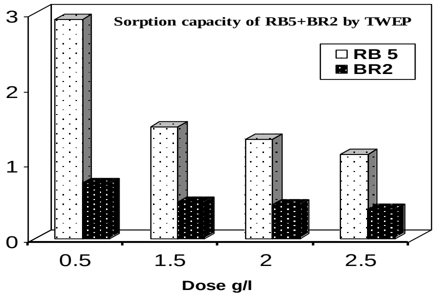
The adsorption capacity for RB5 dye by (TWEP) is higher than adsorption on the BR2. Since (TWEP) bears a positive charge, which it is the major functional group in the adsorption of (RB5). On other hand, (WEP) will inhibit the adsorption of cationic dyes BR2 Fig (4).

Table (1): Effect of (WEP) and (TWEP) doses on removal % of RB 5 + BR2 dye in Binary System with initial concentration 15 ppm at pH 5.83, and equilibrium time 24 hr.

Dose(g/l)	**Binary RB 5+ BR2 (TWEP)**		**Binary RB 5+ BR2 by (WEP)**	
	RB 5	**BR2**	**RB 5**	**BR2**
	Removal %	Removal %	Removal %	Removal %
0.5	26.699	4.927	4.444	33.164
1.5	40.801	9.691	11.408	47.350
2.0	48.334	11.933	13.502	52.153
2.5	51.432	12.959	14.067	53.205

Table (2): Effect of (WEP) and (TWEP) doses on sorption capacity of RB 5 + BR2 dye in Binary System with initial concentration 15 ppm at pH5.83, and 24 hr.

Dose (g/l)	**Binary RB 5+ BR2 (TWEP)**		**Binary RB 5+ BR2 by (WEP)**	
	RB 5	**BR2**	**RB 5**	**BR2**
	Q_e mg/g	Q_e mg/g	Q_e mg/g	Q_e mg/g
0.5	2.923	0.738	0.488	4.965
1.5	1.489	0.484	0.415	2.363
2.0	1.323	0.447	0.370	1.952
2.5	1.126	0.388	0.328	1.773



Fig(4) adsorption capacity for RB5and BR2 dye by TWEP at different dose.

3.2.3.Comparative study of dye sorption in both single and binary dye solutions

The adsorption of C.I. basic red 2 (BR2) and C.I. Reactive blue 5 (RB5) dye solutions by (1.5g/l) (WEP) and (TWEP) were investigated keeping the initial dye concentration (60 and 15ppm) and temperature 25 °C

The high contents of hydroxyl functional groups in (WEP) might form the electrostatic attraction between the (WEP) and cationic dye. C.I. basic red 2 (BR2) can react with OH group in (WEP) to form cell - R – OH --- N^+ BR2. While C.I. Reactive blue 5(RB5) dyestuff, contains SO_3Na group in the molecule can react with quaternary ammonium group in (TWEP) to form cell - R – OH -$N^+(C_2H_5)_2 \cdots SO_3^-$ RB5. As illustrated in Fig.(2), the dye removal efficiency of (BR2) by (WEP) was higher than C.I. Reactive blue (RB5). While (TWEP) have higher adsorption capacity than the (WEP) in the removal of C.I. Reactive blue 5 dye from aqueous solution.

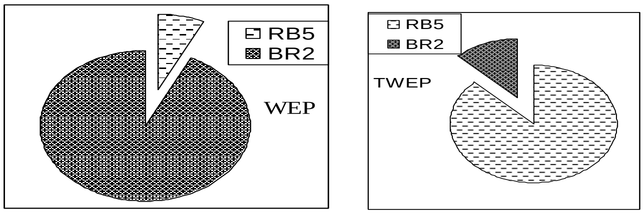


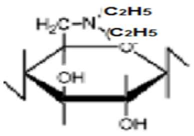
Fig (5) Removal of RB5 and BR2 dyes concentration 60 ppm by (WEP) and (TWEP)

Industry wastewater was normally a mixture of many compounds rather than a single one. In this study, the dye sorption capacities of (WEP) and (TWEP) for BR2 and RB5 were compared in both single and binary dye solutions. Table (1) shows the comparative removal of BR2 and RB5 by (WEP) and (TWEP) in both single and binary dye solutions. From the observation, single BR2 dye adsorbed by (WEP) effectively, with 88.5 % and 55.71 % in single and binary dye solutions, respectively. The composition of (WEP) includes cellulose, hemicelluloses, and lignin contains a large number of hydroxyl groups. As well as the BR2 dye molecules dissociate into positively charged components and adsorb on the binding sites of (WEP) such as hydroxyl groups. However, the removal of RB5 by (WEP) was only 5.42 % and 3.41% in single and binary systems, respectively. The low sorption capacity of RB5 was due to the coulombic repulsion between the anionic dye molecules and the negatively charged surface of the adsorbent.

The (TWEP) showed sorption capability towards single cationic dyes higher than anionic. The percentage of dye removal RB5 by (TWEP) was 97.21 and 60.52 in single and binary systems, respectively. The hydroxyl and –N^+ $(C_2H_5)_2$ groups on the surface of (TWEP) contribute to the binding sites for the adsorption of differently charged dyes.

The elimination procedures for dye can be strongly affected by other constituents of samples. Realistically, in the application of adsorption for the removal of dye ions from textile wastewater there may be a mixture of several dyes. It may mutually enhance adsorption, may act independently, or may interfere with one another. The competitive adsorption is influenced by the interaction of each dye with the surface and with the solvent. The porosity and heterogeneity of the adsorbent are also factors in adsorption. If the dyes are adsorbed at different sites on the adsorbent surface, the total adsorption could be higher than for the individual dye. If they compete for the same sites, there may be a lowering of the total amount adsorbed (**El-Bayaa *et al.*, 2011).**

As shown in Table (3) adsorption values of the binary dye systems C.I. basic red 2 and C.I. reactive blue 5 by (TWEP) respectively were less than those for the single systems. This result indicated that the dye competed with other dye ions for the same sites on adsorbent.The sorption of binary dye molecules by (TWEP) is based on the electrostatic attraction as postulated below:



+ SO_3^- __ RB5 ___ SO_3^- + BR2 __ N^+

TWEP C.I. reactive blue 5 C.I. basic red 2

Scheme 3 the sorption of binary dye molecules by (TWEP)

where SO_3^- – RB5 – SO_3^- represents the structure of C.I. reactive blue 5 and BR2-N^+ represents the C.I. basic red 2 dye ion . According to the conversion scheme above, surface group of TWEP will bind with each dye. These results reinforce an enhancement of the removal of binary dye molecules by TWEP**.**

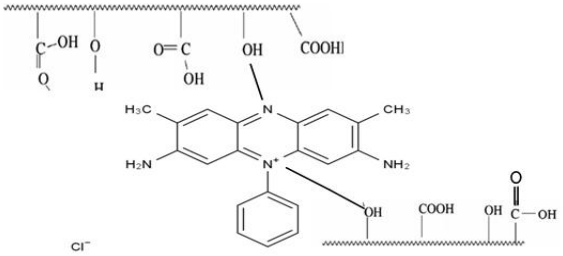
Table 3: The comparative study of single and binary dye sorption by (WEP) and (TWEP) ,[dye] 15ppm and equilibrium time 24 h.

Sorbent	**dye Removal%**			
	C.I. Basic red 2 (BR2) **(single)**	C.I. Reactive blue 5 (RB5) **(single)**	C.I. Basic red 2 (BR2) **(binary)**	C.I. Reactive blue 5 (RB5) **(binary)**
WEP	88.500	5.42	55.71	3.41
TWEP	13.59	97.21	7.37	60.52

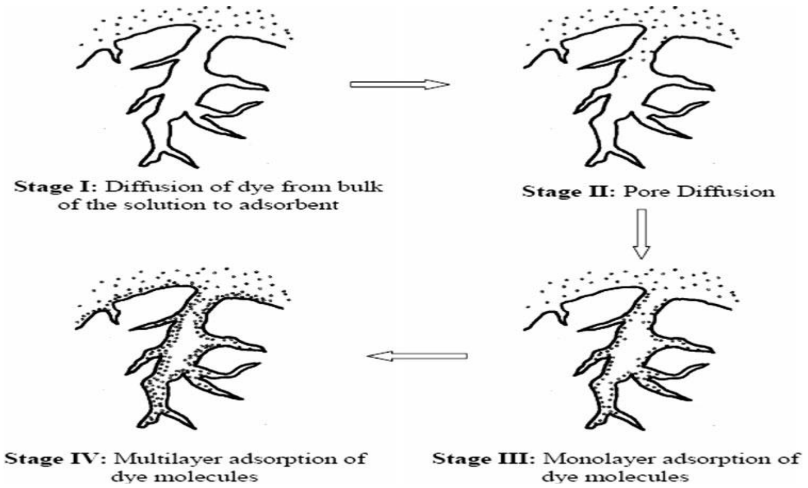
3.3. Mechanism of dye adsorption

The mechanism of adsorbate removal involved four steps: (1) migration of adsorbate molecules from the bulk solution to the surface of the adsorbent; (2) diffusion through the boundary layer to the surface of adsorbent; (3) adsorption at a site; and (4) intraparticle diffusion into the interior of the adsorbent. The solution shaking decreases the boundary layer resistance of the transfer of adsorbate molecules from the bulk solution to the adsorbent surface. Due to this, the adsorbate is forced towards the adsorbent surface and it leads to an increase in the diffusion of adsorbate into the surface of the adsorbent **(Mane et al. 2005).** There were many factors that may influence the sorption behavior, such as dye structure and size, sorbent surface properties, steric effect and hydrogen bonding, van der Waals forces, etc. The structure of the C.I. basic red 2 molecule was a prominent factor for its sorption. The reaction between dye and adsorbent can take place through the weak and strong forces. The weak interactions occur due to the van der Waals forces while the strong interactions occur due to (1) hydrogen bonding interaction between the nitrogen containing amine groups of dye and adsorbent surface (2) hydrophobic– hydrophobic interactions between the hydrophobic parts of dye and adsorbent (3) electrostatic interaction between the cationic dye due to the presence of positively and negatively charged adsorbent surface. A proposed mechanism for the sorption of the C.I. basic red 2 dye onto (WEP) adsorbent is shown in Scheme 4.

Sivakumar and Palanisamy (2010) reported a four-stage adsorption mechanism for removal of Acid Blue 92, Basic Red 29, Reactive Red 4 and Direct Blue 53 by precursor wood Scheme 5.



Scheme 4 Proposed mechanisms for the biosorption of C.I. basic red 2 by (WEP)



Scheme 5.**Proposed four-stage mechanism of dye adsorption**

3.4. Solid state analysis

The waste eggs paper packing dishes (WEP) was analyzed before and after treatment. As well as studies of dye sorption are focused on one-component and competition between dyes for sorption sites before and after adsorption . SEM and IR were used to analyze the morphology and chemical groups of the (WEP) and (TWEP).

3.4.1. Fourier transformed infrared spectroscopy studies

The FTIR of both untreated (WEP) and treated waste eggs paper packing dishes (TWEP) before and after dye sorption are shown in Fig. (6). The FTIR spectra of (WEP) and (TWEP) were recorded between 500 and 4,000 cm^{-1}. The FTIR spectra of (WEP) showed a spectrum indicates bands that appear in the region between 3909.30 and 3449.65 cm^{-1}, which are related to the OH stretching vibrations of the ring and the side chain υ(-CH-OH) and υ(-CH$_2$-OH). Another important vibration in the cellulose spectrum appears in approximately 2904.84 cm^{-1} corresponding to the stretching of the methyl and methylene groups. The band at 3020 cm^{-1} is attributed to stretching of OH group. The band at 1513 cm^{-1} corresponds to aromatic ring vibrations of the phenylpropane skeleton. The peaks at 1270 cm^{-1} and 810 cm^{-1} are attributed to C-O stretching of guaiacyl rings. The band in 1638.28 cm^{-1} corresponds to the vibration of deformation δ (O-H) of primary and secondary hydroxyl groups present in the cellulose structure. The region between 1500–1200 cm^{-1}, shows the presence of bands that also corresponds to the deformation of primary and secondary OH groups; between 1200–1000 cm^{-1} the stretching bands of (C-O) alcoholic groups occur. A series of peaks at 1059.72 cm^{-1}, 1113.12 cm^{-1}, and 1162.70cm^{-1} correspond to C- O- C bonds in the anhydroglucose unit in cellulose. The bands present in the region below 1000 cm^{-1} are assigned to absorptions of the alcoholic groups **Pavia, *et al.*(1996). Silva *et al.*(2011).**

In contrast to TWEP, the bands at 1513 cm^{-1} and 810 cm^{-1} disappeared, and the peak at 3020 cm^{-1} shifted to 3025 cm^{-1}. Moreover, the peak at 2904 cm^{-1} became stronger and a shoulder peak occurred. These peaks indicate that NaOH treatment in the first stage of the synthesis process further removed some soluble lignin in TWEP. Epoxy chloropropane introduced new CH$_2$ groups to the cellulose molecule. There is a new adsorption peak associated with the stretching vibration of C–N band at 1465 cm^{-1}, and a broad band of the skeletal vibration of the quaternary ammonium salt, which was successfully grafted onto the cellulose skeleton **(Cao *et al.*, 2011).**

The FTIR of sorption BR2 by TWEP show unchanged .While the band in 1638.28 cm^{-1} corresponds to the vibration of deformation δ (O-H) of primary and secondary hydroxyl groups present in the cellulose structure shifted to 1630 cm^{-1}. Moreover the band in 3449.65 cm^{-1}, which are related to the OH stretching vibrations of the ring and the side chain υ(-CH-OH) and υ(-CH$_2$-OH) shifted to 3455 cm^{-1} in case of sorption BR2 by WEP Fig (1).

Fig (6) illustrated that adsorption peak associated with the stretching vibration of C - N band at 1465 cm^{-1} shifted to 1470 cm^{-1} in sorption RB5 by TWEP.

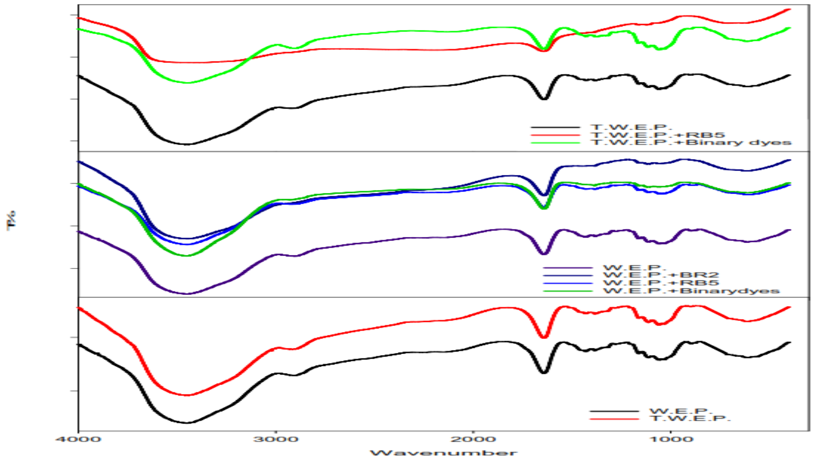
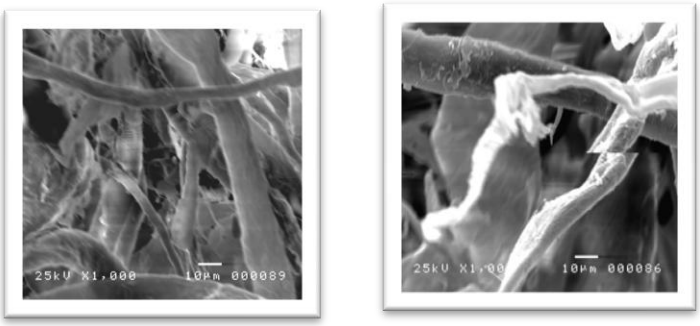


Fig. (6): FT-IR spectrum of both (WEP) and (TWEP),(WEP adsorption by BR2 , RB5 and binary system) and (TWEP adsorption by RB5 and binary system).

3.4.2. Scanning electron microscopy (SEM)

SEM of both untreated (WEP) and treated waste eggs paper packing dishes (TWEP) are shown in Fig. (7 a,b). The color of the (WEP) was dark white, and its fibrous structure looked complicated, while the colors (TWEP) were pale green and their structure looked rigid. It is clearly seen that the surface of TWEP is coarse and rough with some cavities (micro-pores) that contributed to the adsorption of dye in an aqueous solution while WEP appears to have a smoother surface with homogenous creases with some cavities (micro-pores) that contributed to the adsorption of dye in an aqueous solution. It is evident from these images that the surfaces of chemically treated TWEP sorbents have retained their original shape and distribution leading to little or unnoticeable changes. Fig. (8a,b and c) illustrated that scanning electron microscopy of BR2 sorption by WEP and Fig. (9 a and b) represented sorption of RB5 by TWEP in single and binary system.



a-WEP b- TWEP

Fig.(7). SEM of both untreated (WEP) and treated waste eggs paper packing dishes (TWEP)

a-WEP by BR2 b- WEP by RB5 c- WEP by Binary system

Fig.(8). SEM of untreated waste eggs paper packing dishes (WEP) after adsorption BR2 or RB5 a-BR2 , b-RB5 and c- binary system.

a- RB5 by TWEP b- RB5 by TWEP in Binary system

Fig.(9) SEM of treated waste eggs paper packing dishes (TWEP) after adsorption RB5 single and Binary system.

4. Conclusion

The present study results showed that the both untreated (WEP) and treated waste eggs paper packing dishes (TWEP) haves the ability to asorption the dye from the effluent. The pH_{pzc} was found to be 6.8 for (WEP).It was found the removal efficiency increased with increase adsorbent dose. It was also found that the adsorbed species/solute may either block the access to the internal pores or cause particles to aggregate and thereby resulting in the availability of active sites for adsorption. The adsorption capacity for RB5 dye by (TWEP) is higher than adsorption on the BR2. Since (TWEP) bears a positive charge, which it is the major functional group in the adsorption of (RB5). On other hand, (WEP) will inhibit the adsorption of cationic dyes BR2

References

- Acuner.E. and Dilek.F.B.(2004).Treatment of Tectilon Yellow 2G by Chlorella vulgaris., J. Process Biochem., 54: 47-54.
- Akar.E., Altinişik.A. and Seki.Y.(2013). Using of activated carbon produced from spent tea leaves for the removal of malachite green from aqueous solution., J. Ecological Engineering, 52, 19-25.
- Azmi.W., Sani.R.K. and Banerjee.U.C.(1998). Biodegradation of triphenylmethane dyes**.**,J. Enzyme Microbial.Technology., 22, 185-189.
- Cao.w.,Dang.z.,Zhou.x.,Yi.x.,Wu.p. and Zhu.c.(2011).Removal of sulphate from aqueous solution using modified rice straw: Preparation,characterization and adsorption performance.,Carbohydrate polymer,85,571-577.
- ÇiÇek.F., Özer.D. and Özer.A.(2007). Low cost removal of reactive dyes using wheat bran.,J. Hazardous Materials, 146, 408-413.
- Durán.A., Monteagudo.J.M. and Amores.E.(2008). Solar photo-Fenton degradation of Reactive blue 4 in a CPC reactor., J. Environment, 80, 42-48.
- El-Bayaa.A.A., Badawy.N.A., Gamal.A.M., Zidan.I.H. and Mowafy.A.R.(2011).Purification of wet process phosphoric acid by decreasing iron and uranium using white silica.,sand.J.Hazardous Materials., 190, 324–329.
- Fan.L., Zhou.Y., Yang.W., Chen.G. and Yang.F.(2008). Electrochemical Degradation of Aqueous Solution of Amaranth Azo Dye on ACF under Potentiostatic Model.,J. Dyes Pigments,76, 440-446.
- Garg.V.K., Gupta.R., Yadav.A.B.and Kumar.R.(2003). Dye removal from aqueous solution by adsorption on treated sawdust.,Bioresour.Technol. 89:121–124.
- Garg.V.K., Gupta.R., Yadav.A.B. and Kumar.R.(2003). Dye removal from aqueous solution by adsorption on treated sawdust., Bioresour.Technol., 89,121–124.
- Hassanein.F.T. and Koumanova.B.C.(2010).Evaluation of adsorption potential of the agricultural waste, wheat straw for basic yellow 21., *J. Env. Chem. Technol*., 2010, 4594, 407 – 414.
- Hou.M., Ma.C., Zhang.W., Tang.X., Fan.Y. and Wan. H.(2011). Removal of rhodamine B using iron-pillared bentonite., J. Hazardous Materials, 186, 1118-1121.
- Kannan.N. and Sundaram.M.(2001). Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study., Dyes and Pigments,51,25-40.

- Madrakian.T., Afkhami.A. and Ahmadi.M.(2012). Adsorption and kinetic studies of seven different organic dyes onto magnetite nanoparticles loaded tea waste and removal of them from wastewater samples., J. SpectrochimicaActa Part A: Molecular and Biomolecular Spectroscopy., 99, 102-109.
- Mane.S.M., Vanjara. A.K.and Sawant. M.R. (2005). Removal of Phenol from wastewater using date seed carbon. J.Chin. Chem .Soc. 526:1117–1122.
- Mohammed.A.M., Dalia.K.M.and Enas.A.A.(2011).Adsorption of basic dye from aqueous solution using mixture of agricultural solid wastes (maw): isotherm, kinetic studies and process design , *J. Adv. Sci. Eng. Res.*, 2011, 1, 76 – 97.
- Mohan.S.V., Rao.N.C., Prasad.K.K. and Karthikeyan.J. (2002) . Treatment of simulated Reactive Yellow 22 (Azo) dye effluents using Spirogyra species.,J. Waste Management, 22, 575.
- Nikolov.T., Bakalova.N., Petrova.S.and Benadova.R.(2000). An effective method for bioconversion of delignified waste-cellulose fibers from the paper industry with a cellulase complex., Bioresource Technology.,71,1-4.

- Panneerselvam.P., Morad .N. and Tan. K.A.(2011). Magnetic nanoparticle (Fe 3 O 4) impregnated onto tea waste for the removal of nickel (II) from aqueous solution**.,** J. Hazardous Materials, 186, 160.
- Pavia.D.L., Basser.G.M. and Morrill.T.C.(1996). Introduction to Spectroscopy, 2rd ed., Saunders College Publishing, New York.
- Peng.L., Qin.P., Lei.M., Zeng.Q., Song.H., Yang.J., Shao.J., Liao.B. and Gu.J.(2012). Modifying Fe3O4 nanoparticles with humic acid for removal of Rhodamine B in water., J. Hazardous Materials, 193, 209-210.
- Ponnusamy.V., Gunasekar.V. and Srivastava.S.N.(2009). Kinetics of methylene blue removal from aqueous solution using gulmohar (Delonix regia) plant leaf powder: multivariate regression analysis., J.hazardous materials,169, 119 – 127.
- Pons .M.P. and Fuste.C.M .(1993). Uranium uptake by immobilized cells of Pseudomonas strain EPS 5028. Appl. Microbiol. Biotechnol., 39:661–665.
- Shukla.A., Zhang.Y. H., Dubey. P., Margrave. J.L.and Shukla. S. S.(2002). The role of sawdust in the removal of unwanted materials from water. J. Hazardous Materials. 95, 137–152.

- Silva.F.E.C., Silva.L.S., Lima.L.C.B., Santos.J.L.S., Santos.M. R. M. C. and Matos.J. M. E.(2011). Thermodynamic data of 6-(4 -aminobutylamino)-6- deoxycellulose sorbent for cation removal from aqueous solutions., Sep. Sci. Technol.,46, 2566-2574.
- Sivakumar. P. and Palanisamy. N. (2010). Mechanistic study of dye adsorption on to a novel non-conventional low-cost adsorbent., Adv.Appl. Sci. Res.1(1):58–65.
- Sulak.M.T., Demirbas.E. and Kobya.M.(2007). Removal of Astrazon Yellow 7GL from aqueous solutions by adsorption onto wheat bran., J.Bioresource Technology, 98, 2590-2599.
- Sun.L.,Qiao.L.,Sun.S. and Wang.G.(2008).photocatalytic degradation of orange G on nitrogen doped TiO_2 catalysts under visible light and sunlight irradiation.,J. Hazardous Materials., 155, 312-317.
- Tahir.H., Sultan.M. and Jahanzeb.Q.(2009). Remediation of azo dyes by using household used black tea as an adsorbent.,J.African Biotechnol., 1684, 5315-5319.
- Wong.S.Y., Tan.Y.P., Abdullah.A.H. and Ong.S.T.,(2009). The Removal of Basic and Reactive Dyes Using Quartenised Sugar Cane Bagasse., J. Physical Science, 20(1), 59–74.
- Zamouche.M. and Hamdaoui.Q. (2012). Sorption of Rhodamine B by cedar cone: effect of pH and ionic strength.,J.Energy Procedia, 18, 1228-1234.
- Zhong.Q., Yue.Q., Li.Q., Xu.X. and Gao.B.(2011). Preparation, characterization of modified wheat residue and its utilization for the anionic dye removal.,J. Desalination, 267, 193-203.