The removal of cationic dye (Methyl green) dye by adsorbant based Silica gel / Polymer

Fouzia Belaib[1]; Abdeslam-Hassen Meniai[2]

1: Process engineering faculty, Constantine 3 University, Constantine, Algeria, email: belaibfouzia @yahoo.fr

2: Process engineering faculty, Constantine 3 University, Constantine, Algeria, email:meniai@yahoo.fr

Abstract

Polyaniline coated Silica gel was tested as adsorbent for the retention of methyl green dye (MG). in aqueous solution. The adsorption process was carried out batchwise and the effects of key operating parameters such as the contact time, the pH, the initial concentration, the agitation speed and the solid / liquid ratio, on the retention capacity were investigated.

The obtained results showed that the kinetic of the adsorption was of a second order kinetic and the isotherms were better described by the Freundlich model.

The study showed the ability of the polyaniline coated silica gel to retain an organic compound, hence its importance in polluted wastewaters treatments.

Keywords: *Adsorption – Methyl green –Silicagel coated- water treatment–Isotherm.*

I. Introduction

The intensive use of colors either in the everyday life or the industry may be regarded as a potential source of pollution. One can cite as an example the textile industry which is a great user of coloring compounds and therefore inevitably rejects these species which are toxic and hence have to be removed [1]. Several decontamination methods are known, such as Coagulation-Flocculation, Extraction, Ultrafiltration, Ion exchange, Adsorption, etc. [2].

The present work concerns the removal of a coloring compound a cationic dye, namely Methyl green by adsorption onto polyaniline coated silica gel.

II. Experimental and Material

- Adsorbent

Commercial porous silica gel was supplied by PROLABO as spherical particles with diameters ranging from 63 to 200 um, specific area of 500 m^2/g and a porous volume of 75 cm^3 /g. Due to the presence of some trace impurities, mainly carbon and chlorine, a washing of the silica gel with hydrochloric acid, was required and followed by a rinsing in distilled water. The product was dried and stored in a desiccator, ready for further use.

Polyaniline compound was also supplied by PROLABO, with an average molecular weight of 100 g. Bidistilled water was prepared locally using a GFL 2001/4 distillation unit.

- Synthesis of silica – polyaniline support

The chemical synthesis of the polyaniline used as the coating polymer was based on the chemical reaction. It was directly performed on the silica particles by injecting freshly distilled aniline in sealed beaker. The resulting product was filtrated and then washed with hydrochloric acid and then dried at 95°C producing a fine green powder.

Therefore the preparation of the composite colloidal conducting polymer was achieved by means of an in situ deposition of a thin polyaniline film on the silica particles [3].

- Methyl green

Methyl green is a triphenylmethane rosaniline the group derived from hexamethylene para rosaniline It is composed of seven 3 benzene methyl rings tied by a carbon fine powder and is dark green

The physico-chemical characteristics of Methyl Green are :
Molecular weight : 458.47gmol^{-1},

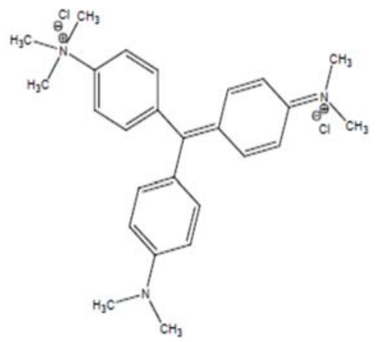

Figure 1: Molecular formula of methyl green ($C_{26}H_{33}Cl_2N_3$)

Spectra UV-Vis solutions are made on a double-beam spectrophotometer SHIMADZU UV-160A (quartz cell) to an area of 200-800 nm is read from a spectrum of 630 nm obtained for an assay result of a dilute solution from the mother solution at pH = 5.9 the figure below Watch the UV visible spectrum. The experiments were conducted in "batch method" (in a single flask of 100 ml) at room temperature (20 ± 3° C) and a stirring rate of 600 rev / min speed. It should be noted that the temperature control was performed by simply reading the thermometer. Also to ensure good dispersion of solid particles of coated Silicagel we adopted the value of 1g / l (or 0.1 g/100 ml) for solid / liquid ratio. Results and discussion the spectrum of the obtained methyl Green natural pH (5.9) and concentration of 10mg / l and it shows the presence of three bands of varying intensity and located successively at 312 nm, 420 nm and 632 nm The absorption spectrum (MG) in the UV visible to acid pH shows a change in the intensity of the wavelength (decrease the intensity de 632nm) and the disappearance of the other two bands seen previously.

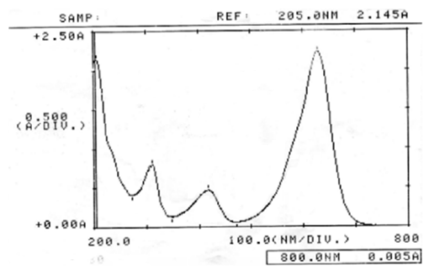

Figure 2: Absorbance spectrum of MG in pH=5.9

in a basic medium (pH = 10), or there was a complete change in the color of the solution, thus turning the (pH = 10), or there was a complete change in the color of the solution, and turning to purple. In addition we found also a total loss of 2 bands [5].

III. Effect of physico-chemical parameters on adsorption capacity of MG dye onto polyaniline coated silica gel

3.1 Contacting time

The study of the adsorption of methyl green on silica gel beads by the polyaniline obviously involves the determination of contact time ,the time corresponding to a state of equilibrium or saturation by the substrate support. The experimental procedure is simple (batch method) and is 30mg to support with 30ml of solution of pollutant. Analysis by UV / Visible spectrophotometry to determine the residual concentrations of the substrate during the sampling performed at different reaction times The dynamic adsorption methyl green illustrated by the figure shown below.

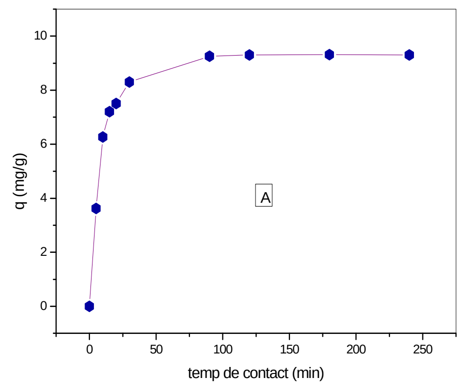

Figure 3 : The effect of contacting time on the retention of MG), (Conditions: C_0 = 10mg / l, V = 600rpm / min, T = 20 ± 3 ° C, r = 10 g / l, pH = 5.9)

equilibrium is quickly reaches the silica gel coated with the polyaniline (adsorption is instantaneous) and the removal rate of the dye is of 78.05%, demonstrating the high affinity of the substrate to the support, or adsorption rate is then rapidly reaches become constant to form a bearing This result was obtained by the ratio

$$q = \frac{(C_0 - C)}{r}) \, V \qquad (1)$$

where q is the adsorption capacity (mg de coloring agent/g adsorbent), C_0 and C are the initial and final adsorbate concentrations, respectively in (mg/l), m the mass of adsorbent(g), V the volume of the solution (l) and r the solid to liquid ratio (g/l).

3.2 pH effect

The initial pH of the solution is an important parameter that must be taken into account in any adsorption study. The adsorption capacity of the dye on the silica gel was determined over a pH range of from 2 to 10. From the results shown in Figure, it appears to be clear that the pH of the aqueous solution to effect a significantly dye retention (MG) by two supports. The maximum amount of adsorbed dye occurs at pH 10 with 96% removal of dye.

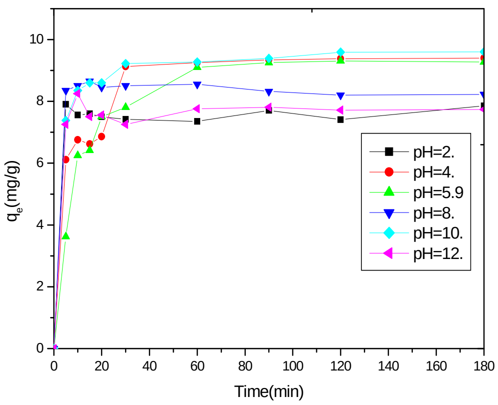

Figure 4: The effect of pH on the retention of MG) (Conditions: C_0 = 10mg / l, V = 600tr / min, T = 20 ± 3 ° C, r = 10 g / l)

3.3 The effect of initial concentration

the influence of the initial concentration of the methyl green in the adsorbing process and processed on in the adsorbing process and processed on was studied in the range of 10 to 80mg / L while maintaining the other parameters constant (T = 20 ± 3C °, pH = 5.9, V = 600rpm/min) on the retention capacity of the solid support.

The results obtained are shown in the following figure:

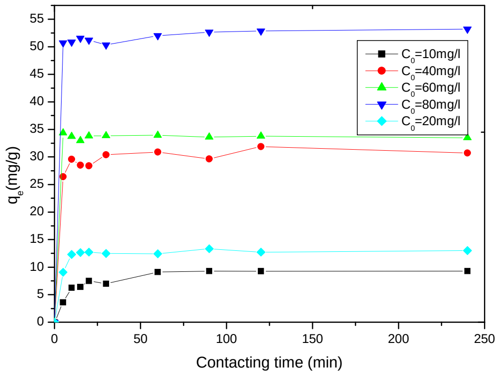

Figure 5: The effect of initial concentration of (MG) (Conditions: pH=5,9 , V = 600 rpm / min, T = 20 ± 3°C, r = 10 g / l)

The adsorption capacity of the dye in solution increases with increasing initial concentrations of the dye in the solution. Increasing the concentration of induced elevation drive strength of the concentration gradient thus increasing the diffusion of dye molecules in solution into the surface of the adsorbent if it so the concentration of the Methyl Green in the solution is high, there will be more of molecules that diffuse to

the surface sites of the support particles therefore the retention means becomes larger increasing the retention of the substrate

3.4 Effect of the temperature

The effect of the elevation of temperature on the retention of methyl green is illustrated in Figure 6 or there is a significant improvement in adsorption equilibrium this is recorded as and when the temperature rises over the increasing effect of the reaction temperature (20 ° C to 45 ° C and 65 ° C), the amount of the pollutant adsorbed increases to a concentration of 10mg / l Moreover, the kinetics of adsorption also seem to evolve with increase of the temperature. Arguably the adsorption phenomenon is a phenomenon thermo dependent this may be due to an increase of the relative mobility which improves dye exposure sites active adsorption on the one hand and sent to sites inaccessible. High energy contribution to overcome the repulsive forces located at the interfaces of solid liquid

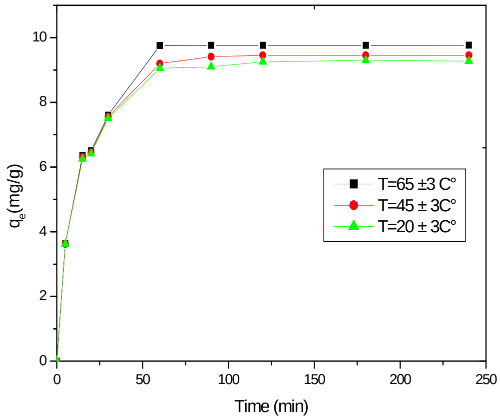

Figure 6: The effect of initial concentration of (MG) (Conditions: Co = 10mg/l, pH=5.9, V = 600 rpm, T = 20 ± 3 °C, r = 10 g / l)

4. Kinetic study

The kinetic models were applied to sorption kinetic data in order to investigate the behavior of adsorption process of dye onto silica gel. These models are the pseudo –first –order and pseudo – second order .

4.1 Pseudo-first-order model

The pseudo-first-order model was described by the following equation:

$$\log (q_e - q_t) = \log (q_e) - k_1\, t/2.303 \qquad (2)$$

where q_e and q_t refer to the amount of dye adsorbed (mg g-1) at equilibrium and at any time, t (min), respectively and k_1 is the equilibrium rate constant of pseudo first-order adsorption (min^{-1}).

4.2. Pseudo-second-order model

The pseudo-second-order model is represented by the following equation:

$$t/q_t = 1/k_2\, q_e^2 + t/q_e \qquad (3)$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g mg_{-1} min_{-1}).

Experimental kinetic data were adjusted according to the indicated models Table4 showed that the first order equation model provided the best correlation with experimental results. This fact indicates that adsorption of methyl green on silica gel coated with the polyaniline follows second order model (R^2=0.99923)

Table 1: The correlation factors and the kinetics constants of the two kinetic models of MG

Model	First order kinetic		Second order kinetic	
Support	K_1	R^2	K_2	R^2
Silicagel	0.0245	0.923	0.1705	0.9993

5. Adsorption Isotherms

To plot the adsorption isotherms, the evolution of the equilibrium capacity was followed, based on residual concentrations in the aqueous phase. We have used different values of concentration. To identify the real nature of the adsorption process we tested models of Langmuir, Freundlich.
The linear forms of each model are given by the following expressions:

$$\text{Log}q_e = \log k_f + 1/n \log c_e \qquad (4)$$

$$1/qe = 1/q_{max} + 1/kq_{max}c_e \qquad (5)$$

q_e: adsorption capacity at equilibrium (mg / g).
q_{max}: adsorption capacity at saturation (mg /g) and correspond to the formation of a monolayer.
K_L: adsorption coefficient.
K_f : the adsorption constant,
1/n : Constant of adsorption intensity

$$\ln Qe = \ln K_f + 1/n_f . \ln C \qquad (6)$$

5.1 BET isotherm

This admits newer model training multilayer adsorbate and also makes the phenomenon of saturation. It involves the solubility of the solute in the solvent, in the form of its saturation concentration. It is represented by the following equation:

$$Q/Q_m = k(C_e/C_0) / (1 - C_e/C_0)\, [1 + (k-1)\, C_e/C_0] \qquad (7)$$

with Q: the capacity retention (mg / g)
Q_m: the ability of mono-molecular retention (mg /g)
C_e: the equilibrium concentration (mg / l)
C_o: Initial concentration (mg / l)
K: constant adsorption

The linear form of this equation is given by the following equation:

$C/(Q(C_0-C)) = 1/ (Q_m k) + (k-1)/(k Q_m) [C/C_o]$ (8)

The Main parameters characterizing each model, are summarized in Table 3

Table 3: Isotherm adsorption of MG onto Polyaniline coated Silica gel

Models	**Constants**	**R^2**
Langmuir	Q_{max}=7.6557 K_L=3.3813	0.9557
Freundlich	K_f=1.26325 n_f=5.1993	0.9600
BET	Q_{max}=4.1673 K=4.167	0.8750

The results of Table 3 show clearly that the retention of methyl green on silica gel is well described with Freundlich Model. These results are confirmed with the correlation factor of R^2=0.96009.

Conclusion

The present study showed that effectively polyaniline coated silica gel can be used to eliminate, methyl green dye, a coloring agent, widely used in the textile industries. The optimum pH value was equal to 6. The MG adsorption onto Silica gel coated followed the second order kinetics and the process was best represented by the Freundlich isotherm.

References

[1] T. Sauer G., Gesconeto HJ.J and Moreira, R. F.

P.M., 149 (2002) 147-154.

[2] Yang N, Zhu S, Zhang D, Xu S (2008), Synthesis and properties of magnetic Fe3O4-activated carbon nanocomposites particles for dye removal. Mater. Lett. 62:645–647

[3] Baghriche .O, K. Djebbar, *Asian J. Chem*., 18 (2006)11

[4] F. Belaib, A-H Meniai, M. Bencheikh lehocine, A. Mansri, M. Morcellet, M. Bacquet, B. Martel, 'A Macroscopic study of the retention capacity of copper by polyaniline coated onto silica gel and natural solid materials', Desalination 166(2004)371-377

[5] Bhatnagar A. and Jain A.K., A comparative adsorption study with different industrial wastes as adsorbents for the removal of cationic dyes from water, J. Colloid Interface Sci., 2005, 281, pp49-55