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Adsorption of brilliant green by poly (ethylene terephthalate) grafted acrylic acid /acryl amide fiber-isotherm study

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ABSTRACT

A fibrous adsorbent was prepared by grafting Acrylic acid /Acryl amide co-monomers onto poly(ethyleneterephthalate) fibers. The resulting sorbent has been studied for removal of trace brilliant green from aqueous solution. The optimum pH value for sorption of the brilliant green was 6. The sorption capacity of functionalized fiber is 65.5 mg g^{-1}. Scatchard analysis revealed that the homogeneous binding sites were formed in the polymers. The equilibrium adsorption data of brilliant green on modified fiber were analyzed by Langmuir, Freundlich, Temkin and Redlich–Peterson models. Based on equilibrium adsorption data, the Langmuir, Freundlich and Temkin constants were determined 0.032 (m^3 kg^{-1}), 4.92 (mkg kg^{-1}) (m^3 kg^{-1})$^{1/n}$ and 1.777 (L g^{-1}) at pH 6 and 20 °C, respectively. Based on Redlich–Peterson Isotherm analysis, Langmuir isotherm best-fit the equilibrium data for adsorption of brilliant green.

Keywords: Isotherm study, poly (ethylene terephthalate)-grafted-Acrylic acid /Acrylamide Fiber, Brilliant green, polymer grafting, pigment removal

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INTRUDUCTION

One trend in modern civilization is to effect gradual replacement of natural materials with either all synthetic materials or modified natural materials. In the polymeric age, it is essential to modify the properties of a polymer according to tailor-made specifications designed for target applications. There are several means to modify polymers properties, viz. blending, grafting, and curing. 'Blending' is the physical mixture of two (or more) polymers to obtain the requisite properties.[1] 'Grafting' is a method wherein monomers are covalently bonded (modified) onto the polymer chain, whereas in curing, the polymerization of an oligomer mixture forms a coating which adheres to the substrate by physical forces.

Fibrous reactive materials have a very high adsorption capacity due to their very large surface area.[2] There are mainly two ways to prepare reactive fibers, namely, the exchange of the existing groups on the fiber with other reactive groups having higher adsorption ability and grafting of various vinyl monomers upon the fiber by graft copolymerization. Grafting improves the adsorption capacity and selectivity of fiber significantly by forming many reactive groups upon the polymer chains.

Brilliant green (BG) is a triphenylmethane dye, originally used as a dyeing agent in the textile industry, has also been widely used in the fish farming industry for many decades. The reason for its popularity is derived from its broad antimicrobial spectrum and effectiveness in the prevention and treatment of certain fish diseases compared to other fishery chemicals [3] On the other hand, it is also used as a dye in silk, wool, and jute and in leather cotton, paper, and acrylic industries.[4] However, BG has now become a highly controversial compound due to the risks it poses to the consumers of treated fish, including its effects on the immune system and reproductive system and its genotoxic and carcinogenic properties.[5-9] The most widely used methods for removing dyes from wastewater systems include physicochemical, chemical, and biological methods, such as flocculation, coagulation, precipitation, adsorption, membrane filtration, electrochemical techniques, ozonation, and fungal decolorization.[10] Adsorption is widely used in the removal of contaminants from wastewaters. The design and efficient operation of adsorption processes require equilibrium adsorption data. The equilibrium isotherm plays an important role in predictive modeling for analysis and design of adsorption systems.[11]

The purpose of the present study is to indicate the feasibility of grafted poly AA/AAm on PET fiber as a sorbent for removal of brilliant green from aqueous solution. For this purpose, the adsorption isotherms like Langmuir, Freundlich, Temkin and Redlich–Peterson models were studied for sorption behavior of this new sorbent.

MATERIALS AND METHODS

2.1. *Reagents and solutions*

Fiber PET (filaments: 130 and dtex 170) made in Textile Engineering Department, Amir Kabir University of technology, Tehran, Iran. Acrylic acid, acryl amid, benzoyl peroxide, acetone, NaH_2PO_4, Na_2HPO_4, CH_3COONa, HNO_3, CH_3COOH and brilliant green were products of Merck (Darmstadt, Germany).

All the reagents were analytical grades and used without any further purification.

The 0.01 M acetic acid - acetate buffer (pH 3 – 6.5), 0.01 M phosphate buffer (pH 6.5 - 9) were used to adjust the pH of the solutions, when needed.

2.2. *Synthesis of PET-AA/AAm fiber*

Details of the preparation and characterization of the MIP was reported in the previous work. [12] Fiber samples (0.100 ± 0.001 kg^{-3}) were placed in a 0.01 cm^3 polymerization tube and calculated amount of AA and AAm were added to it. Then Bz_2O_2 dissolved in 3 cm^3 acetone was added to tube. The mixture was made up to 50×10^{-3} m^3 with deionized water and placed into a water bath at the polymerization temperature 85±1 ºC. The fiber samples taken at the end of polymerization were freed from homopolymer or copolymers by washing with boiling water and acetone for 1 h (changing the washing water four times). The washed fiber was dried at 50 ºC under vacuum.

2.3. *Batch method*

A sample solution (50×10^{-6} m^3) containing (0.3×10^{-9} kg m^{-3} of Brilliant green was taken in a glass stopperd bottle, and the pH was adjusted to optimum value. The 0.1×10^{-3} kg of PET-AA/AAm fiber was added to the bottle and the mixture was shaken for optimum time. The fiber was taken out and sorbed brilliant green was determined by UV-Vis spectroscopy at 624 nm in supernatant.

2.4. *Isotherm studies*

Isotherm studies were carried out by adding a fixed amount of adsorbent (0.1×10^{-3} kg) to a series of beakers filled with 50 (cm^3) diluted solutions of brilliant green ($10\text{-}100\times10^{-6}$ kg m^{-3}). The beakers were then sealed and placed in a water bath shaker and shaken at 200 rpm with a required adsorbent time (4 h.) at 20 °C and optimum pH. The beakers were then removed from the shaker, and the final concentration of brilliant green in the solution was measured by UV-Vis spectroscopy at 624 nm. The amount of brilliant green at equilibrium q_e (mkg kg^{-1}) on PET-AA/AAm fiber was calculated from the following equation:

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

where C_0 and C_e (µkg m^{-3}) are the liquid phase concentrations of brilliant green at initial and equilibrium, respectively, $V\times10^{-3}$ (m^3) the volume of the solution and $W\times10^{-3}$ (kg) is the mass of adsorbent used.

RESULTS AND DISCUSSION

3.1. *Brilliant green sorption as a function of pH*

The degree Brilliant green sorption at different pH values was determined by batch equilibration technique. A set of solutions (the volume of each 100×10^{-6} m^3) containing 0.5×10^{-3} kg m^{-3} of Brilliant green was taken. Their pH values were adjusted in range 3-9 with 0.01M acetate and/or phosphate buffer solutions. The 0.1×10^{-3} (kg) of PET-AA/AAm fiber was added to each solution and the mixture was shaken for 6 h. The optimum pH values for quantitative uptake of metal ions were ascertained by measuring the brilliant green content (by UV-Vis spectroscopy) in supernatant liquid. The optimum pH range for the sorption of the metal ion is shown in Fig.1. The maximum sorption was occurred at pH 6.

3.2. *Total sorption capacity*

The 0.1×10^{-3} kg of PET-AA/AAm fiber were stirred for 4 h with 50×10^{-6} m^3 solution containing $10\text{-}100\times10^{-3}$ kg m^{-3} of brilliant green at optimum pH and 20 ºC. The dye concentration in the supernatant liquid was estimated by UV-Vis spectroscopy. The sorption capacity of the sorbent for the brilliant green was ascertained from the difference between the dye concentrations in solution before and after the sorption. The saturated adsorption capacity of the fiber was shown in Fig.2. This figure indicates the effect of initial concentration of the brilliant green in the solution on capacity sorption of brilliant green by PET-AA/AAm fiber. The capacity goes up with increasing initial concentration of the brilliant green in the solution. The capacity adsorption of the modified fiber was found 65.5×10^{-3} kg kg^{-1} in initial dye concentration of 100×10^{-3} kg cm^{-3}.

3.3. *Sorption ability*

The amount of sorption of brilliant green in aqueous solution acrylic acid /Acryl amide grafted poly (ethyleneterephthalate) fibers is compared with that of free poly(ethyleneterephthalate) fibers. The result was shown in Fig 3. This Fig demonstrates the amount of brilliant green in solution after sorption of PET-AA/AAm fiber is much less than PET fiber. The sorption ability of grafted PET fiber is 14% more, in comparison with non-modified PET fiber.

3.4. *Adsorption isotherms*

The Langmuir equation is given in the following form:[13]

$$q_e = q_{max}.K_L.\ C_e/\ (1+K_L.C_e) \qquad (2)$$

where q_{max} is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mkg kg^{-1}) and K_L is the Langmuir constant (m^3 kg^{-4}). The equation (2) can be rearranged to a linear form:

$$C_e/q_e = (1/q_{max}.K_L) + (C_e/q_{max}) \qquad (3)$$

The constants can be evaluated from the intercepts and the slopes of the linear plots of C_e/q_e versus C_e (Fig. 4).

Conformation of the experimental data in to Langmuir isotherm model indicates the homogeneous nature of PET-AA/AAm fiber surface. Langmuir parameters calculated from Equation (3) are listed in Table 1.

The essential characteristics of the Langmuir equation can be expressed in term of a dimensionless separation factor, R_L, defined as:[14]

$$R_L = 1 / (1+K_L.C_0) \qquad (4)$$

Table 1 shows the value of R_L (0.238) is in the range of 0-1 at optimum pH which confirms the favorable uptake of the brilliant green.

The Freundlich equation is an empirical equation employed to the described heterogeneous systems, in which it is characterized by the heterogeneity factor 1/n. Hence, the empirical equation can be written as:[15]

$$q_e = K_F.\ C_e^{\ 1/n} \qquad (5)$$

where K_F is the Freundlich constant (mkg kg^{-1}) (m^3 kg^{-4}) $^{1/n}$ and 1/n is the heterogeneity factor. A linear form of the Freundlich expression can be obtained by taking logarithms of the Equation (5):

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (6)$$

Therefore, a plot of ln q_e *versus* ln C_e (Fig. 5) enables the constant K_F and exponent 1/n to be determined. The Freundlich equation predicts that the Brilliant green concentration on the adsorbent will increase so long as there is an increased in the Brilliant green concentration in the liquid.

The Temkin equation suggests a linear decrease of sorption energy as the degree of completion of the sorptional centers of an adsorbent is increased.

The Temkin isotherm has been generally applied in the following form:

$$q_e = \frac{RT}{b}\ln(AC_e) \quad (7)$$

and can be linearized:

$$q_e = B \ln A + B \ln C_e \quad (8)$$

where B=RT/b and b is the Temkin constant related to heat of sorption (J mol^{-1}). A is the Temkin isotherm constant (m^3 kg^{-1}), R the gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K). Therefore plotting q_e versus ln C_e (Fig. 6) enables one to determine the constants A and B. Temkin parameters calculated from Equation (7 and 8) are listed in Table 1.

The Redlich–Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. The Redlich–Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. It can be described as follows:

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (9)$$

It has three isotherm constants, namely, *A*, *B*, and *g* ($0 < g < 1$), which characterize the isotherm. Its limiting behavior is summarized as follows:
Where $g = 1$

$$q_e = \frac{AC_e}{1 + BC_e} \quad (10)$$

i.e. the Langmuir form results.

Where constants *A* and *B* are much greater than unity[16]

$$q_e = \frac{A}{BC_e^{g-1}} \quad (11)$$

i.e. the Freundlich form results.

Where $g = 0$

$$q_e = \frac{AC_e}{1 + B} \quad (12)$$

i.e. the Henry's Law form results.

Eq. (9) can be converted to a linear form by taking logarithms:

$$\ln\left(A\frac{C_e}{q_e}-1\right)=g\ln(C_e)+\ln(B) \qquad (13)$$

Three isotherm constants, *A*, *B*, and *g* can be evaluated from the linear plot represented by Eq. (13) using a trial and error procedure, which is applicable to computer operation. It was developed to determine the isotherm parameters by optimization routine to maximize the coefficient of determination, R^2, for a series of values of *A* for the linear regression of ln(*C*e) on ln[*A*(*C*e/*q*e)−1] and to obtain the best value of *A* which yields a maximum 'optimized' value of R^2 using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel.

The Redlich–Peterson isotherm constants, A, B, and g as well as the coefficient of determination, R^2, for the sorption of brilliant green on to PET-AA/AAm fiber using the linear regression is shown in Table 1. It can be seen that the values of g were close to unity, which means that the isotherms are approaching the Langmuir form and not the Freundlich isotherm. The result shows that the Langmuir isotherm best-fit the equilibrium data for adsorption of Brilliant green on PET-AA/AAm fiber.

3.5. *Scatchard analysis*

Scatchard analysis was employed to further analyze the binding isotherms. The Scatchard equation can be expressed as, $Q/C= (Q_{max}–Q)/K_d$, where C (µmol· cm^{-3}) is the equilibrium concentration of brilliant green; Q (µmol· kg^{-4}) is the equilibrium adsorption amount at each concentration; Q_{max} (µmol kg^{-4}) is the maximum adsorption amount; and K_d (µmol L^{-4}) is the equilibrium dissociation constant at binding sites. Fig. 7 shows the Scatchard plots of the binding of brilliant green to the fiber. It is clear that the Scatchard plot for fiber is a single straight line. The linear regression equation was $Q/C= –10.188Q + 3806.1$ (R^2=0.9543), suggesting that the homogeneous recognition sites for brilliant green were formed in the SPE fiber. From the slope (–10.188 ($1/K_d$)) and intercept (3806.1 (Q_{max}/K_d)), K_d and Q_{max} for the affinity binding sites were calculated to be 0.098 µmol· m^{-9} and 373.6 µmol·kg^{-4}, respectively.

Table 1: Isotherm parameters obtained by using linear method

Langmuir isotherm model			
q_{max} / mkg kg^{-1}	K_L / m^3 kg^{-1}	R_L	R^2
0.125	0.032	0.238	0.9599
Frendlich isotherm model			
K_F / (mkg kg^{-1}) (m^3 kg^{-1})$^{1/n}$		n	R^2
4.92		1.32	0.9914
Temkin isotherm model			
A / L g^{-1}	B	b / J mol^{-1}	R^2
1.777	20.523	118.76	0.9514
Redlich–Peterson isotherm model			
g	B / (m^3 kg^{-1})^g	A / m^3 kg^{-4}	R^2
0.963	0.047	4.4	0.9440

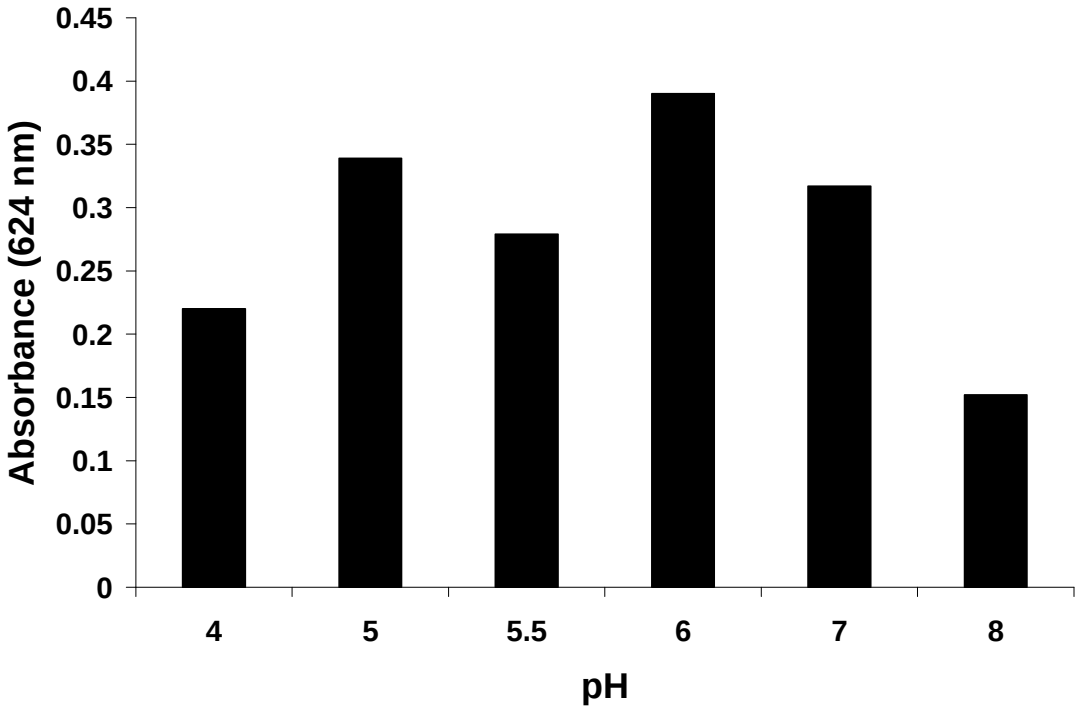

Fig. 1. Effect of pH sorption of brilliant green onto PET-AA/AAm

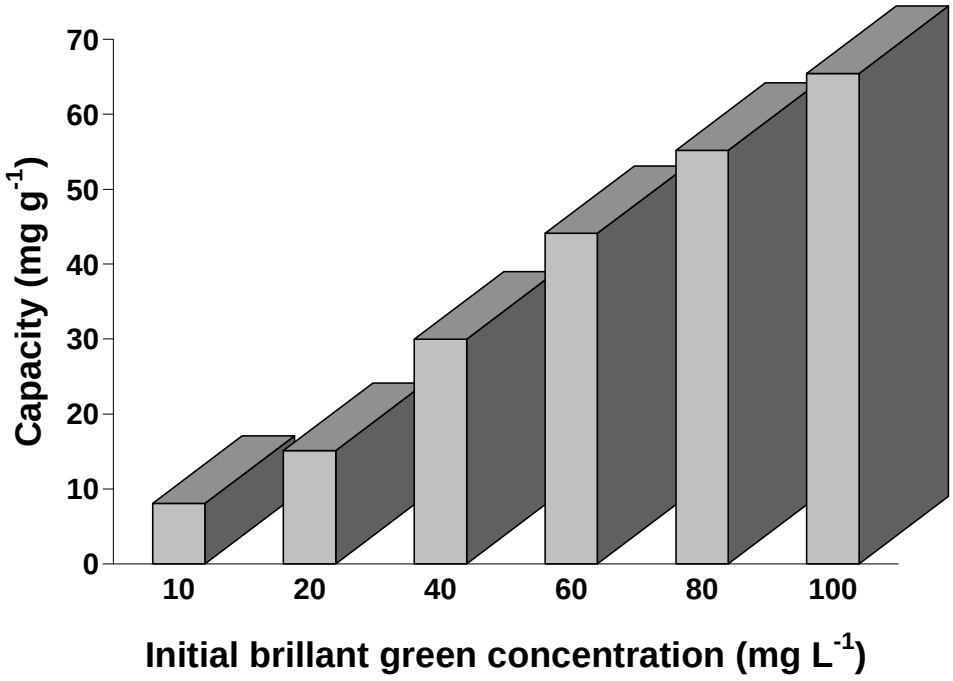

Fig.2. Effect of initial concentration of the brilliant green in the solution on capacity sorption of brilliant green onto PET-AA/AAm

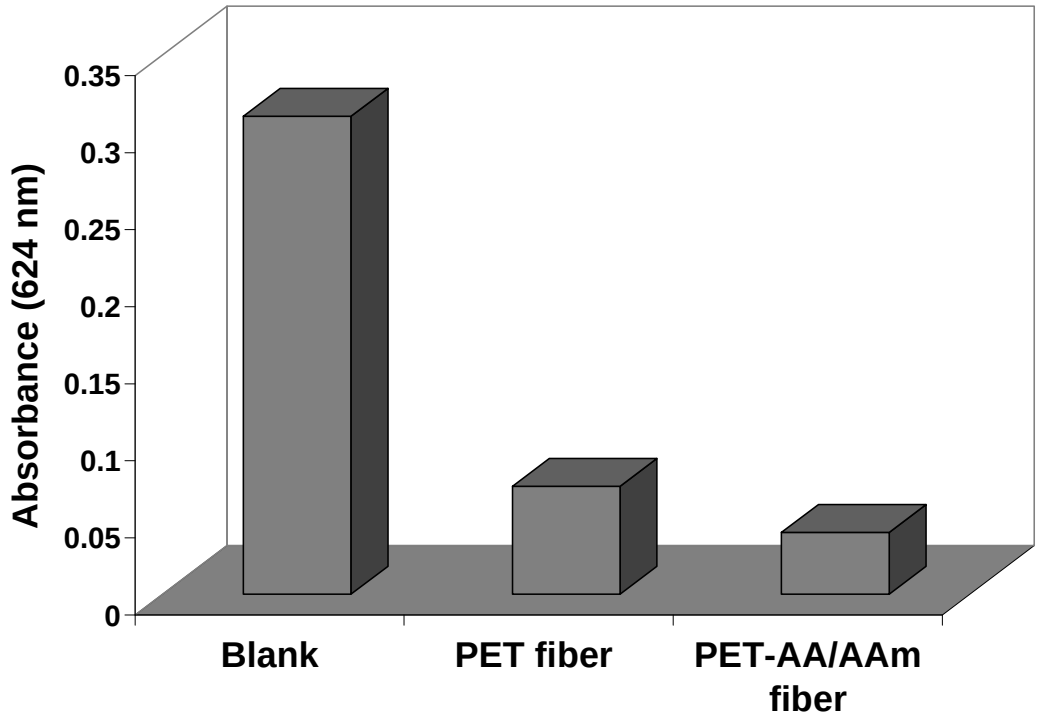

Fig.3. Sorption ability of PET-AA/AAm fiber and PET fiber

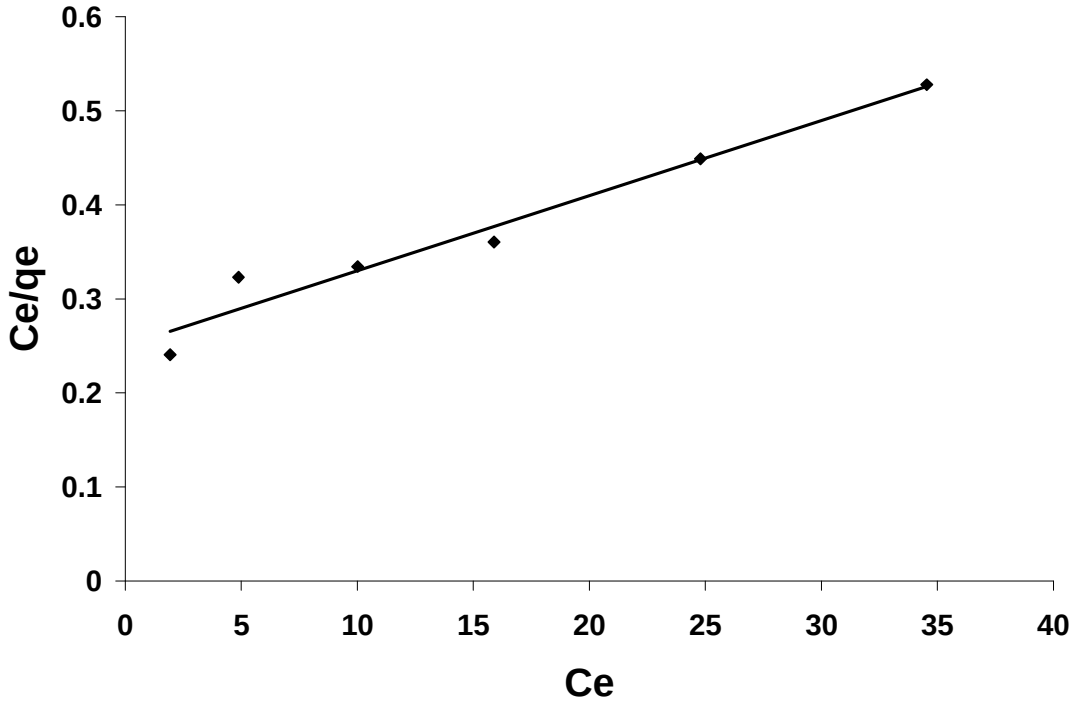

Fig.4. Langmuir isotherm for brilliant green adsorption onto PET-AA/AAm at 20 °C

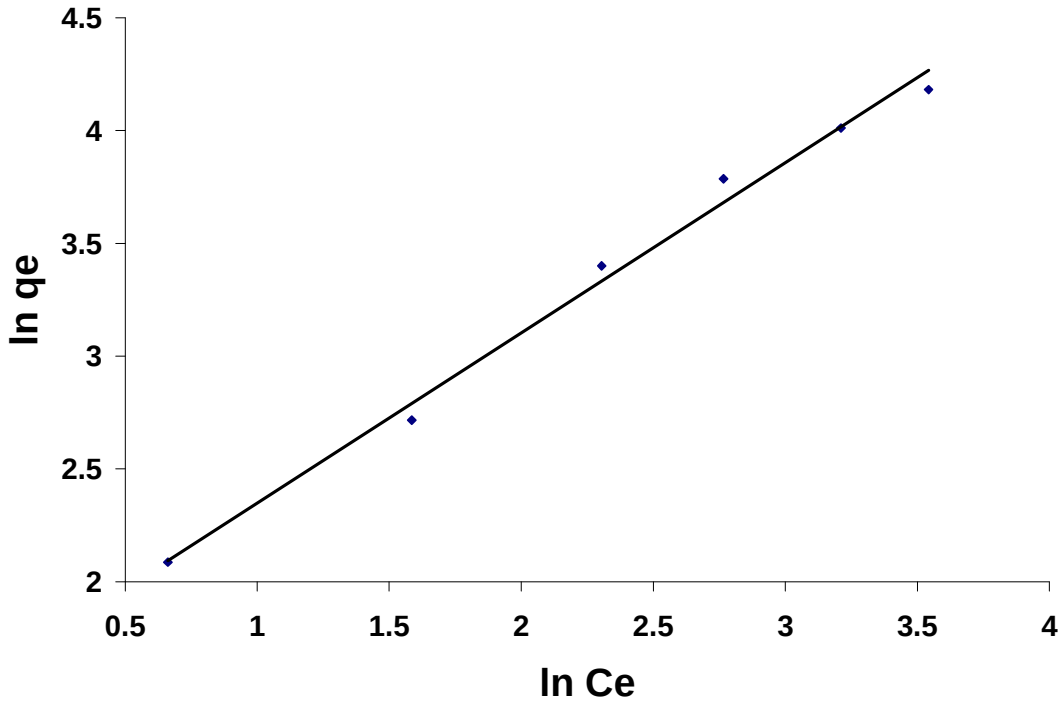

Fig.5. Freundlich isotherm for brilliant green adsorption onto PET-AA/AAm at 20 °C

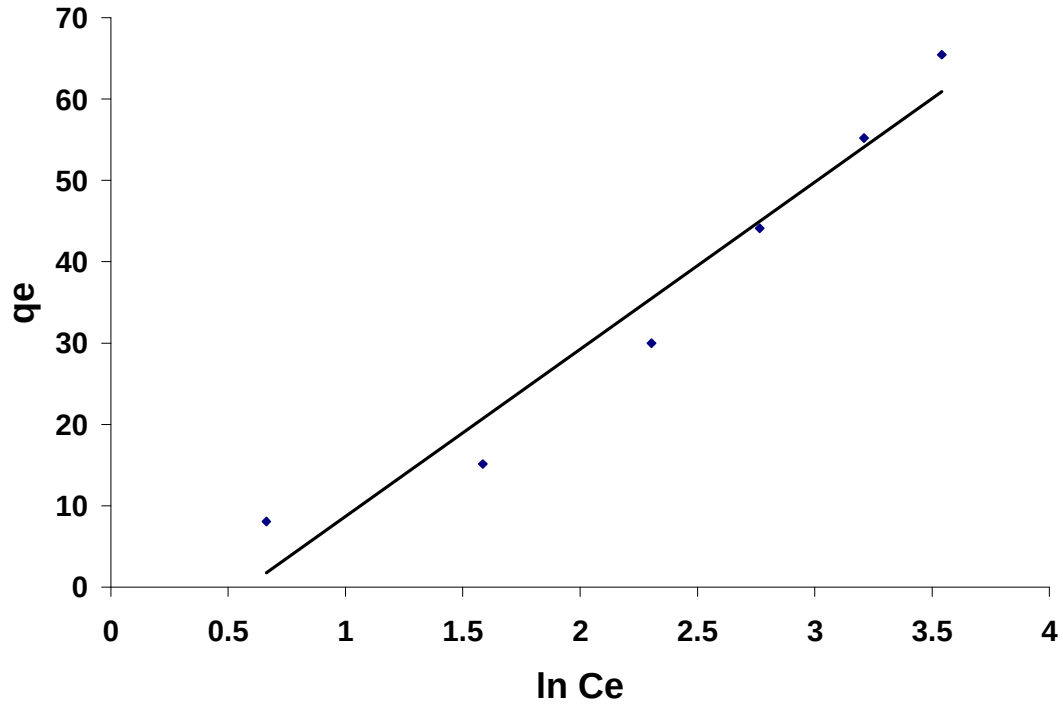

Fig.6. Temkin isotherm for brilliant green adsorption onto PET-AA/AAm at 20 °C

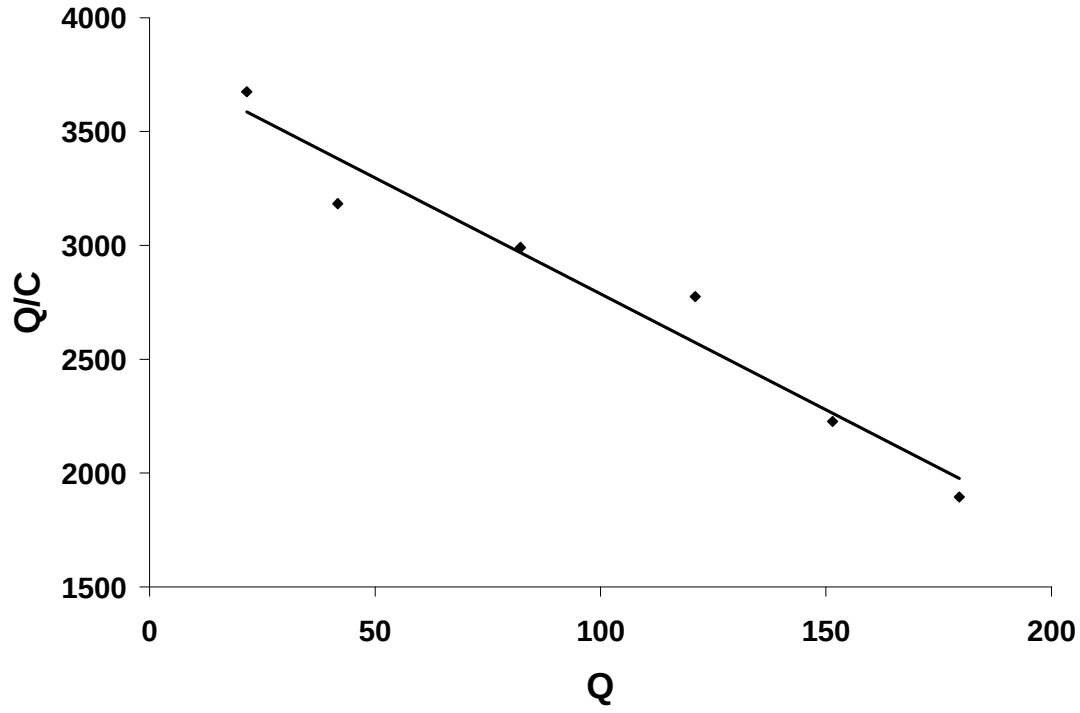

Fig. 7. Scatchard plots of brilliant green adsorption onto PET-AA/AAm at 20 °C

CONCLUSION

A new fibrous adsorbent was prepared by grafting Acrylic acid /Acryl amide comonomers onto poly (ethylene terephthalate) fibers. The synthesis of the fiber is simple and economical. The fiber has a good potential for removal of trace amount of brilliant green from large sample volumes. Based on the Langmuir isotherm analysis, the monolayer adsorption capacity was determined to be 0.125×10^{-3} (kg kg^{-1}) at 20 °C. The R_L values showed that the PET-AA/AAm fiber was favorable for the adsorption of brilliant green.

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