Adsorption of Dye Benzoazurin-G (organic contaminants) by Poly Vinyl Activated Charcoal derived from *Eichhcornia* (water weeds)

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Abstract

The industries produce highly colored large volume of waste water, which is one of the major environmental problems. Such dye effluent is toxic and difficult to remove by conventional waste water treatment methods. Adsorption has evolved into one of the most effective physical processes for removal of dyes. The most commonly used adsorbent for dye removal is activated carbon, because of its capability for efficiently adsorbing a broad range of different types of adsorbate. The aim of present work is to study the effectiveness of the adsorbent to removal of synthetic dye from textile waste water using low cost adsorbents prepared from Eichhcornia. The adsorption of Dye Benzoazurin-G in aqueous solution on various low cost adsorbents was analyzed. The adsorption of dyes by activated charcoal obtained from plant material (Eichhcornia) was studied and was found to be very effective at pH 8. The effect of various parameters such as contact time, adsorbent dosage, initial dye concentration and pH has been studied. Adsorption of dye Benzoazurin-G is highly pH dependent and the results indicate that the maximum removal (93.6%) took place at dose 8gm/l in the pH range of 8 and initial concentration of 40 ppm. Kinetic experiments reveal that the dilute dye solution reached equilibrium within 105 min. The adsorbent capacity was also studied the dye adsorption followed both the Langmuir and Freundlich equation isotherms. Comprehensive characterization of parameters indicates that PVAC-Eic. to be an excellent material for adsorption of dye Benzoazurin-G to treat wastewater containing low concentration of the dye.

Key words: Adsorption, Eichhcornia, Adsorption isotherms, Adsorption kinetics.

1. INTRODUCTION

The industries produce highly colored large volume of waste water, which is one of the major environmental problems. Population explosion, rapid urbanization, industrial and technological expansion, energy utilization and waste generation from domestic and industrial sources have rendered many waters unwholesome and hazardous to man and other living resources. Of various pollutants contained in industrial wastewater, colour is considered to be very important from the aesthetic point of view and is stated as 'visible pollutant. Almost every industry uses coloring matter to colour their products. Unspent coloring materials are usually discharged, with/without treatment into the aquatic environment. Dyes are highly coloured polymers and low biodegradable. Colour/dye being one of the important recalcitrant, permit for long distances in flowing water, retards photosynthetic activity, inhibit the growth of aquatic biota by blocking out sunlight and utilizing dissolve oxygen and also decrease the recreation value of stream. Nowadays concern has increased about the long-term toxic effect of water containing these dissolved pollutants.

Various treatment methods for removal of dyes from industrial effluents like coagulation using alum, lime, ferric chloride, ferric sulphate, chemical oxidation methods using chlorine and ozone and membranes separation methods are in vogue [1]. Many of them don't operate at low concentration of coloured compounds in the effluent. Therefore special measures are necessary to be taken to remove them from the effluents. Adsorption has received considerable attention for colour removal from wastewaters as it offers the most economical and effective treatment method. Low cost adsorbents like fly ash, coal, peat[2], sawdust[3], lignite and wood have received considerable interest because of their local availability and their practically low cost[4]. Use of bio-adsorbent like rice husk[5], coconut coir, banana pith[6] wheat straw, baggase, saw dust[7], used tea leaves, cow dung [8], have been found to be highly effective, cheap and eco-friendly.

The objective of present article reports the feasibility of utilizing *Eichhcornia* charcoal as a low cost adsorbent material for the removal of Dye Benzoazurin-G from waste water. *Eichhcornia* is an example of water weed plant. They are mainly composed of ligno-cellulose materials, and its charcoal have relatively large surface areas that can provide intrinsic adsorptive sites to many substrates and can inherently adsorb waste chemicals such as dyes and cations in water due to the columbic interaction and physical adsorption.[9]

2.MATERIALS AND METHODS

2.1 Preparation of Poly Vinyl Activated Charcoal from Eichhcornia leaves:

The naturally dried leaves of the plant Eichhcornia was obtained locally. Leaves were first subjected to heating process known as carbonization in which fixed carbon was formed, which was then activated by heat- leaves treatment (200-1600oC). Washing with Phosphoric acid, Zinc chloride etc to activates it. It was cut into small pieces. The leaves were treated with concentrated sulphuric acid (five times its volume) and kept in oven at 150°C for 24 hours. It was filtered and washed with distilled water repeatedly to remove sulphuric acid (washing tested with two drops of barium chloride solution) and finally dried. The adsorbent was sieved to 40-60-mesh size and heated at 150 °C for 2 hours.

Poly Vinyl Alcohol is a good hydrophilic polymer and has water adsorbent capacity. 1 gm of PVA was dissolved in 10ml hot water (10% solutions) as a result gel formation occurs. Now 2.5gm of furnace black was added in it to form a thick paste. This paste was then mixed with activated carbon obtained from the leaves of Eichhcornia. Now the thick paste obtained was then dried to form lumps. The lumps were further ground into fine powder. This powder was then used as an adsorbing material. When 2.5gm Furnace Black was used the results were better.

2.2 Preparation of Stock Solution of Benzoazurin-G:

In order to have wastes of uniform characteristics and to avoid interferences of other dyes the synthetic stock solution of waste water was prepared from AR Grade chemical. The stock solution of dye Benzoazurin-G was prepared by dissolving 1.000gram in 1000ml of double distilled water to give 1000ppm solution.

The different range of test solution of different concentration of dye solutions was prepared from stock solution which varied between 40-150ppm.

Na^+ $\dot{O}^-$

2.3 Experimental methods and measurement

The experiments were carried out in the batch mode for the measurement of the adsorption capacities the Bottles with 250ml were filled with wastewater and adsorbent. The bottles were capped and shaken at room temperature on an electric shaker at 500rpm for required time period. The separation of the adsorbent and solution was carried out by centrifugation. The concentration of the unabsorbed benzoazurin-G dye in the solution was determined spectrophotometrically. Bach adsorption studies were carried out to study the effect of pH (3, 4, 5, 6,7and 8), contact time (10-140 min), adsorbent dose (2-10 g/l) and initial Dye concentration (40-150ppm) at room temperature using stopper bottles. The initial pH of solution was adjusted by using 0.05 N HCl or 0.1N NaOH without changing the volume of the sample. After agitating the sample for the required contact time, the contents were centrifuged and filtered through what man No.41 filter paper and unreacted dye in the filtrate was analyzed spectrophotometerically.

The removal efficiency (E) of adsorbent was defined as:

$$E (\%) = [(C_o – C_e) / C_o] \times 100$$

Where Co and Ce is the initial and equilibrium concentration of dye solution (mg/l), respectively.

Influence of each parameter (pH, initial dye concentration, and adsorbent particle size and carbon concentration) was evaluated in an experiment by varying parameter under evaluation while all the parameters in the experiments were maintained as constant.

3. Sorption isotherms

Equilibrium studies that give the capacity of the adsorbent and the equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms which are usually the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium. Freundlich and Langmuir isotherms are the earliest and simplest known relationships describing the adsorption equation. These two isotherms model were used to assess the different isotherms and their ability to correlate experimental data.

3.1 Langmuir isotherm

The Langmuir equation was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. This model is based on two assumptions that the forces of interaction between adsorbed molecules are negligible and once a molecule occupies a site and no further sorption takes place. The saturation value is reached beyond which no further sorption takes place. The saturation monolayer can then be represented by the expression:

$$Ce/qe = 1/Qob + Ce/Qo$$

Where, Ce is equilibrium concentration (mg/I), q is the amount at equilibrium time per unit adsorbent (mg/g) and Q and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The essential characteristics of Langmuir isotherm can be described by a separation factor11, which is defined by,

$$R_L = 1/1 + b\ Co$$

Where Co is the initial adsorbate concentration (mg/l) and b is the Langmuir constant (mg/l). Values of dimensionless equilibrium parameter RL (0.99711) show the adsorption to be favorable (0< RL<1). More ever the higher correlation coefficient value (R2=0.976) confirmed the suitability of the modal.

3.2 Freundlich Adsorption Isotherm:

The Freundlich isotherm model was chosen to estimate the adsorption intensity of the sorbent towards the adsorbent. It is an empirical equation employed to describe the isotherm data given by:

$$qe = K_F (Ce)^{1/n}$$

The linearized form of the Freundlich equation use for analysised and it is given as;

$$\text{Log } qe = \log K_F + 1/n \log Ce$$

K_F and n are Freundlich constants; n gives an indication of the favorability and kf the capacity of the adsorbent. The values of 1/n, less than unity is an indication that significant adsorption takes place at low concentration but the increase in the amount adsorbed with concentration becomes less significant at higher concentrations and vice verse. The higher the K_F value, the greater the adsorption intensity. The value of 1/n, less than unity was obtained mostly for the AC-E. Also the K_F value, the greater the adsorption intensity. Present study verifies value of 1/n (0.577999) & value of K_F (1.97696) from table (1).

The equilibrium concentration was calculated using following formula

$$Ce = C0 - (\%\ adsorption \times C0 / 100)$$

The amount of dye adsorbed per unit weight of an adsorbent 'q' was calculated using following formula

$$q = (C0 - Ce) \times V / m$$

Where Ce is the equilibrium concentration (mg/l) and qe the amount adsorbed (mg/g) at equilibrium time; C0 is the concentration (mg/l), m is the mass of the adsorbent (gm) and V is the volume of the solution (L).

The correlation coefficient (R2) for Freundlich and Langmuir isotherms are merely equal. The correlation coefficient (R2) for Freundlich (0.999) & Langmuir (0.976) were obtained from Table (2). Therefore for the present adsorption study it can be stated that Freundlich and Langmuir adsorption equations are found to be better fitted. ($R2 \approx 0.999$)

4.Result and Discussion:

4.1 Effect of contact time:

In adsorption system, the contact time play a vital role irrespective of the other experimental parameters, affecting the adsorption kinetics. Figure 1 depicts that there was an appreciable increase in percent removal of dye Benzoazurin-G up to 105 min. thereafter further increase in contact time the increase in removal was very small (at 120 min). Thus the effective contact time (equilibrium time) is taken as 105 min. and it is independent of initial concentration (40ppm).

4.2 Effect of pH:

pH is an important parameter influencing dye adsorption from aqueous solutions. It affects both the surface charge of adsorbent and the degree of ionization of the dye in solution. The influence pH of solution on the extent of adsorption of adsorbent material used is shown in figure-2 .The removal of dye from solution by adsorption is highly dependent on the pH of the solution. It was found that 93.6 % removal of dye Benzoazurin-G achieved at pH 8 and thereafter the percent removal decreases with increases in pH as 10and 12. Thus the optimum adsorption pH for removal of dye was found to be 8.

4.3 Effect of adsorbent dose: The effect of adsorbent dose on percent removal of dye Benzoazurin-G is shown in Figure 3 Adsorbent dose was varied (2, 4, 6, 8, 10gm/l) and performing the adsorption studies at pH 8. The present study indicated that the amount of dye adsorbed on PVAC- Eic increase with increase in the Eichhcornia dose up to 8gm/l and thereafter further increase in dose the increase in removal was very small. Thus the effective dose is taken as 8 gm/l.

5. Conclusion:

Pollution of the aquatic environment with toxic valuable dye is widespread. Consideration of the modes of purifying these contaminations must be given to strategies that are designed to high thorough put methods while keeping cost at minimum. Adsorption readily provides an efficient alternative to traditional physiochemical means for removing dye. In conclusion, Eichhcornia could be used as potential adsorbent for the removal of dye from aqueous solutions. The optimium data were found from this adsorption studies is given below in table:

REFERENCES:-

1. Namasivayam, C., Kadirvelu, K**.,(1994)**:Coir pith as an agricultural waste by-products, for the treatment of dyeing wastewater. – Bioresource Techno 48, pp. 79-81.
2. Raghuvansi, S.P. Raghav, A.K.Singh, R. and Chandra, A **(2002)**: Investigation of Saw dust as Adsorbent for the Removal of Methylene Blue in Aqueous Solution, In Proceeding of International Conference for Water and Wastewater- Perspectives in Developing Countries, (WAPDEC), International Water Association, U.K., pp 1053-1062.
3. Singh, R.P., Singh Y., Gupta, N.,Gautam, A.,Singh, S.,Chauhan, M.S., Kulshresta, R.R., Bhati, M., June**(2001)**: Decolonization of water containing Crystal Violet, Methylene Blue, Malachite Green and Rhodamine B using activated carbon, fly ash, baggase and baggase.-Proc. 10th National Symposium on Environment India, pp. 143-147.
4. Anjaneyulu Y., Himabindu, V**.(2001)** :Application of mixed adsorbent (oxygenated coconut shell, activated carbon, -OCSAC – Flyash-china clay)
5. For the removal of basic dyes from Industrial effluents. J Envt and Pollt **8(1)**, 117-127.
6. Deo, N., Ali, M., (1993) : Dye adsorption by new low cost material Congo Red – Indian J Envtl Prot 13 **(7)**, pp. 496-508.
7. Namsivayam, C., Kadirvelu, K., **(1997)**: Activated carbon prepared from coir pith by physical and chemical activated methods. –Bioresource Technol. **62** (3), pp. 123-127.
8. Singh, R., **(2001)**: COD reduction from the Textile waste water using bio-adsorbents, from the aqueous solutions. M.Tech thesis, Dept. of Environmental Sciences and Engg, Jambheshwar University, Hisar, Haryana, India.
9. TENG, Hsisheng and HSIEH, Chien-To. s coal.*Industrial and Engineering Chemistry Research*, September**1998**, vol. **37**, no. 9, p. 3618-3624.
10. SUN, Gang and SHI, Weixing.*Industrial and Engineering Chemistry Research*, April **1998**, vol. **37**, no. 4, p. 1324-1328

Table-1

Sr No.	Particular	Optimium data (PVAC-Eic)
1	Time (min.)	105 min
2	pH	8
3	Dose (gm/l)	8 gm/l
4	Max. % removal of Dye	93.6%

Table -2

Langmuir and Freundlich constants for adsorption of Benzoazurin-G:-

Dose (gm/l)	Freundlich isotherm (linear equation)	Langmuir isotherm (linear equation)	R2 Freundlich	R2 Langmuir
8	y=0.578x+0.296	y=0.044x+0.842	0.999	0.976

Table -3

Langmuir and Freundlich constants for adsorption of Benzoazurin-G:-

Dose (gm/l)	Freundlich constants			Langmuir constants		
	Kf	n	1/n	Qm (mg/g)	b (l/ mg)	RL
8	1.97696	1.730104	0.577999	22.77727	0. 052257	0.99711

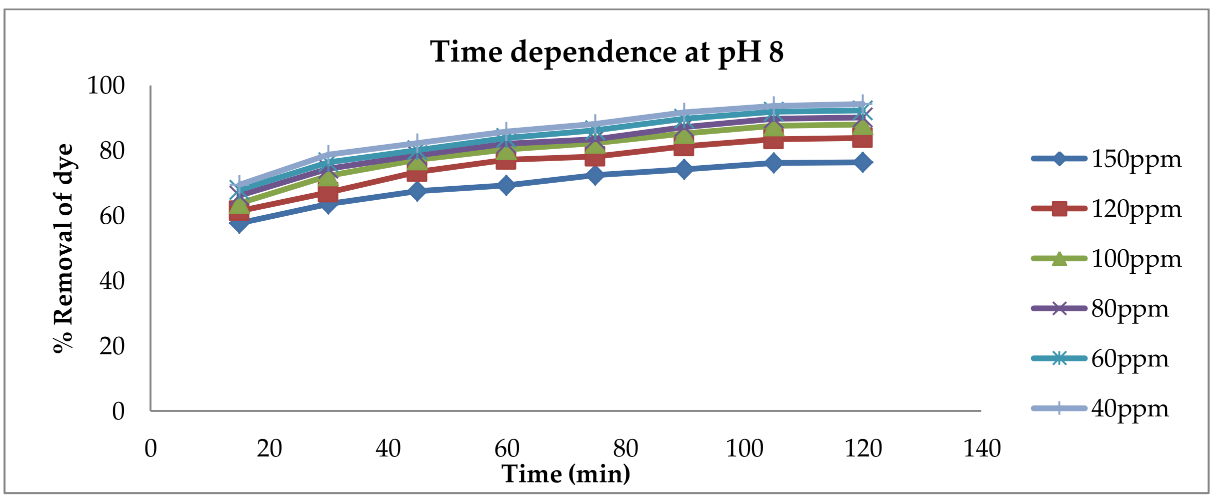

Figure 1: Effect of contact time on removal of Dye Benzoazurin-G at different concentration by PVAC-Eic. at pH 8

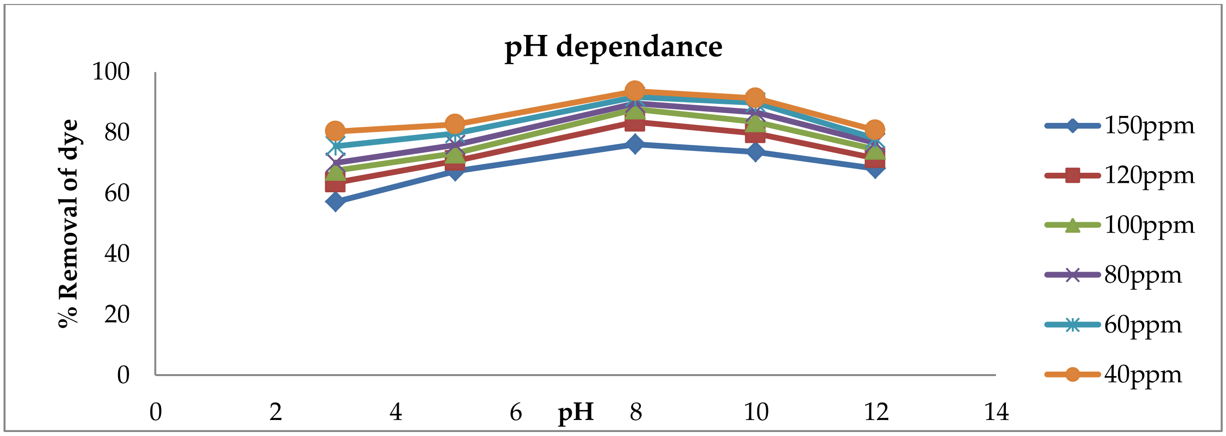

Figure 2: Effect of pH on removal of Dye Benzoazurin-G at different concentrations by 8gm/l of PVAC-Eic. at constant contact time 105 min.

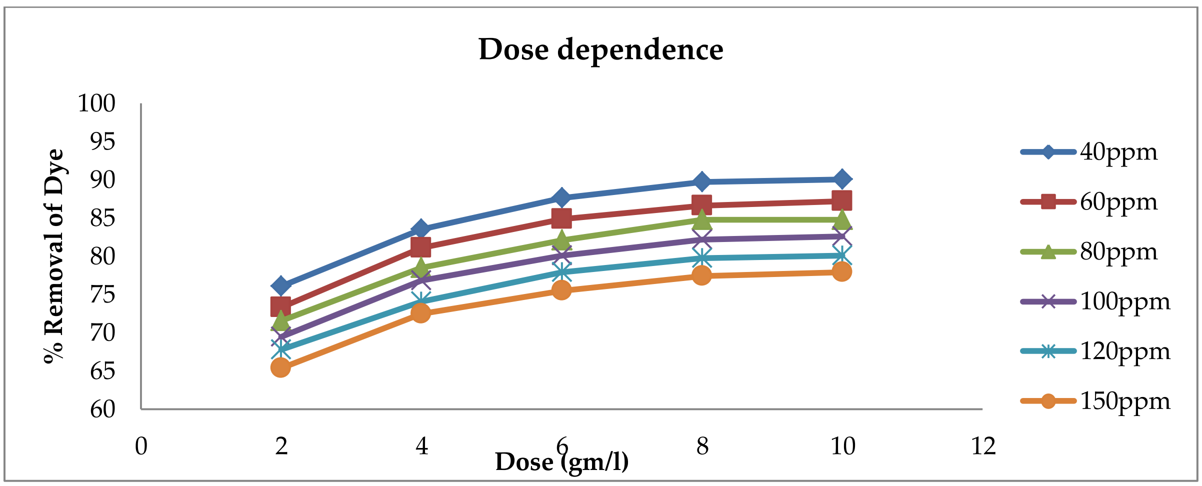

Figure 3 : Effect of PVAC-Eic. dose on percent removal of Dye at equilibrium contact time 105 min. and effective at pH 8.

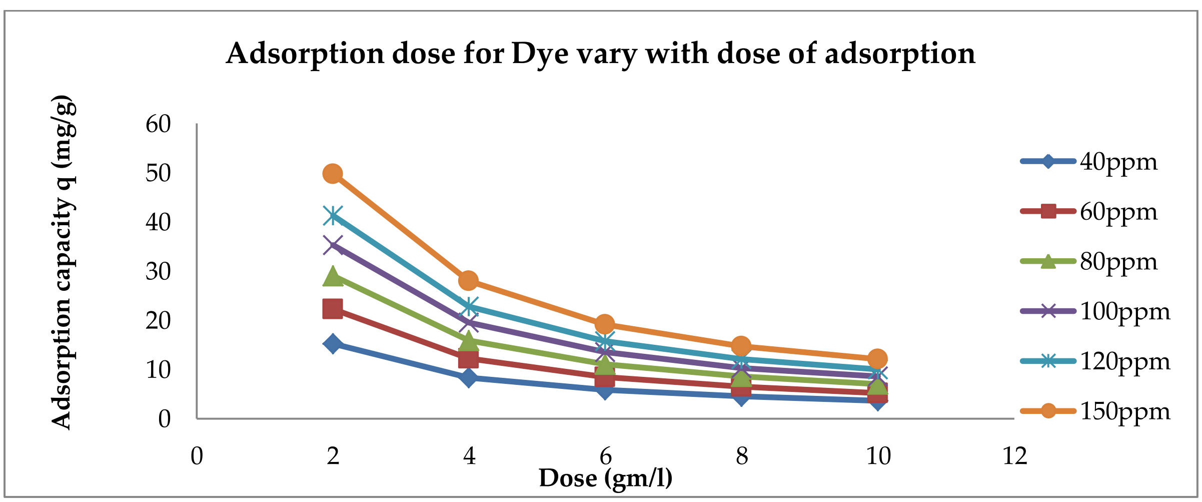

Figure 4: Effect of dose of adsorbent on adsorption capacity at equilibrium contact Time 105 min and effective pH 8.

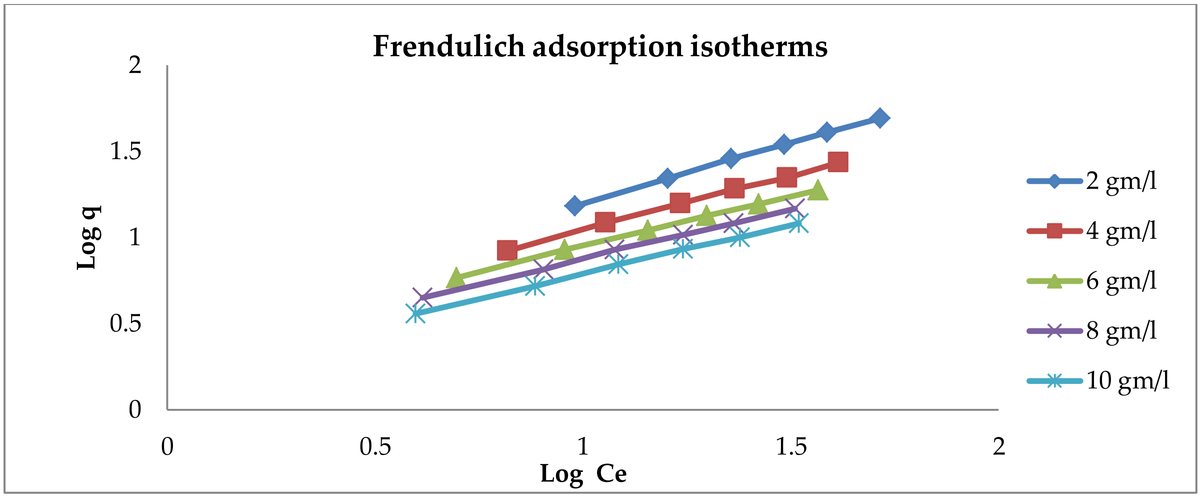

Figure 5: Freundlich Isotherm plot for Dye Benzoazurin-G adsorption by PVAC-Eic. at optimum conditions

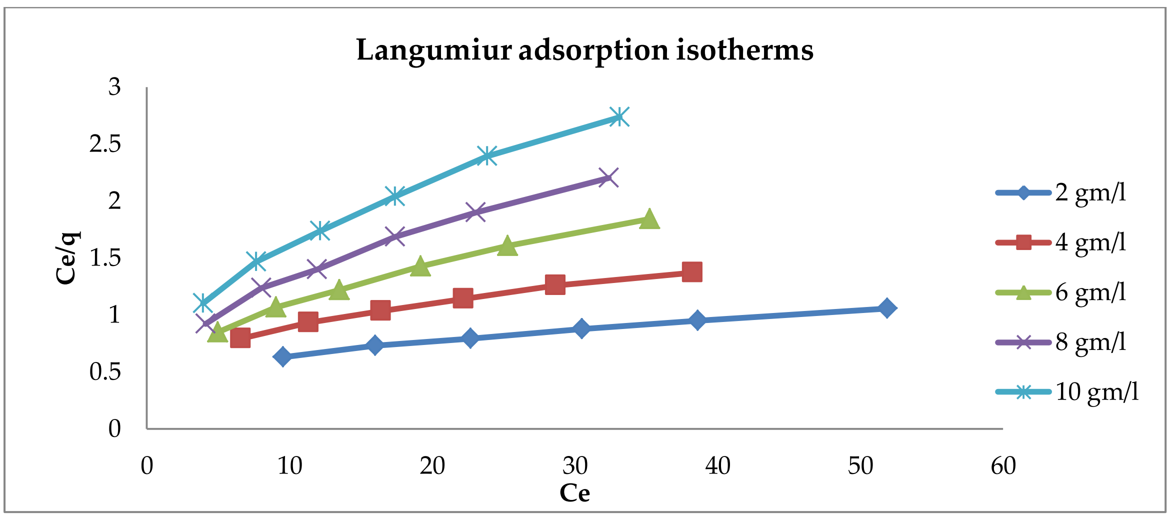

Figure 6: Langmuir Isotherm plot for dye Benzoazurin-G adsorption by PVAC-Eic. at optimum conditions.