

Adsorption of Methyl Red on Coal Fly Ash from Aqueous Solution

Beruk A. Bekele* Muluneh A. Balcha Feleke B. Demelash
Addis Ababa Science and Technology University, College of Biological and Chemical Engineering, Addis Ababa, Ethiopia

Abstract
The discharge of highly colored effluents into natural water bodies is aesthetically displease impedes light penetration, as a result disrupt biological processes within stream and thus treatment is required before discharge into a water body. In the present study, coal fly ash generated from coal based thermal power plant has been used as low-cost and effective adsorbent for the removal of methylene red dye from an aqueous solution. Chemical treatment of coal fly ash was carried out before adsorption with 10% sulfuric acid to improve its surface area. The influence of adsorbent dose, initial dye concentration and contact time at room temperature and pH of 6.8 on removal of the dye has been studied. It was found that, percentage removal of the dye increases by increasing adsorbent dose, initial dye concentration and contact time. The optimum condition of contact time, adsorbent dose and initial dye concentration found were 120 min, 1 g and 25 mg/L respectively. Adsorption data was fitted well on both Langmuir and Freundlich Isotherm models.
Keywords: Methyl red dye, Adsorption, Coal fly ash, Isotherm models

1. Introduction

There are more than 100,000 commercially available dyes with over 7×10^5 tons of dyestuff produced annually (Carmen et al., 2012; Farman et al., 2015;). These dyes are widely used in industries such as textile, rubber, pulp and paper, plastic, cosmetic and leather. Among these various manufacturing industries, the textile industry is one of the most complicated industries and ranks first in usage of dyes for coloration of fiber (Kanawade et al., 2011). A single dyeing operation can use a number of dyes from different chemical classes resulting in a complex wastewater. Color stuff discharged from this industry poses certain hazards and environmental problems (Adib et al., 2017). Methylene red is one of the most commonly available dye in textile industries which is toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities; mutagenic and carcinogenic(Kant, 2012; Ramesh, 2013; Shah et al., 2013). This colored compound is not only aesthetically displeasing but also inhibit sunlight penetration into the stream and affect aquatic ecosystem (Maria, 2014). Moreover, methylene red dye has complex aromatic molecular structures, synthetic origin and recalcitrant nature which make it more stable and difficult to biodegrade (Kumar et al., 2013). There are various conventional methods of removing dyes. These include coagulation and flocculation, oxidation or ozonation and membrane separation. However, these methods are not widely used due to their high cost and economic disadvantage (Durairaj et al., 2012; Tahir et al., 2012). The conventional wastewater treatment, which rely on aerobic biodegradation also have low removal efficiency for reactive and other anionic soluble dyes. Due to low biodegradation of methylene red dye, a convectional biological treatment process is also not very effective in treating textile wastewater. In contrast, adsorption technology has gained a wider application due to its inherent low cost, simplicity, versatility and robustness for removal of this dye from the waste sewage as well as its sludge free clean operation (Bada et al., 2008; Farman et al., 2015; Kanawade et al., 2011; Mehta et al., 2014; Nadu, 2011). The most common adsorbent materials for adsorption process such as alumina, silica, metal hydroxides and activated carbon require high cost (Sareen et al., 2014). Furthermore, regeneration produces additional effluent as well as loss of adsorbents and its uptake capacity (Kanawade et al., 2011). This leads to further studies for cheaper or cost-effective substitutions of commercially available adsorbents which had been used to remove the dye.

Coal Fly ash which is a waste substance derived from thermal power plants, steel mills, etc. It is one of the cheapest and commercially available material for possible replacement (Bada et al., 2008; Dwivedi, Jain et al., 2015; Jain et al., 2016; Kumar et al., 2013; Sareen et al., 2014). Since wide scale coal firing for power generation began in the 1920s, many million tons of ash have been produced (Dwivedi et al., 2015; Farman et al., 2015).

The present study mainly focuses on the study of the factors in the removal of methylene red from textile industry wastewater by utilization of coal-fly-ash as a potential adsorbent. The effects of initial dye concentration, adsorbent dose, and contact time on adsorption capacity of coal fly ash as well as study on adsorption isotherm models were examined.

2. Materials and Methods

2.1. Materials

The reagents used in the study were HCl (33% assay) and NaOH (99.5%), Sulfuric acid (99.5%), methylene red dye ($C_{16}H_{18}N_3SCl.3H_2O$).

2.2. Instruments

UV-visible spectrophotometer (Shimadzu 1800), oven, pH meter, centrifuge and magnetic stirrer were used for this study.

2.3. Methodology

2.3.1. Activation of coal fly ash

Coal fly ash was taken from IKA Addis textile industry plc. The collected coal fly ash was sieved to a desired particle size of below 150 µm. 100 g of sieved coal fly ash was washed with warm distilled water (60˚C) for 5 minutes to remove the adhering organic materials. The sample was mixed and soaked in diluted solution of sulfuric acid (10% wt.) for 12 hr in the ratio of 1 g to 2 ml (Bada et al., 2008).This soaking of coal fly ash was done overnight. After soaking, the ash sample was filtered and washed again with distilled water until the pH increase to 7.0. Then the sample was dried in an oven and heat treated at 105oC for 6 hr for adsorbent activation purpose. After treatment, the sample was stored in a plastic bag until needed for experiment.

2.3.2. Batch adsorption experiment

1000 ppm of methylene red dye stock solution was prepared and the pH adjusted to 6.8 using 0.1 M HCl and 0.1M NaOH. Batch adsorption experiments were then conducted by diluting from the stock solution. The effect of initial concentration, adsorbent dose, and adsorption time were investigated at three different levels. 150 ml of dye solution with different methylene red concentrations of 25 mg/l, 50 mg /l and 75 mg/l were prepared in 250 ml Erlenmeyer flasks from the stock solution. Treated coal fly ash samples with adsorbent dose of 0.5 g, 1 g and 1.5 g were weighted. Depending on the order of experiment obtained from experimental design, the weighted coal fly ash samples were dosed into the prepared dye solutions and mixed using magnetic stirrer for the maximum time of 120 min. During mixing, samples were taken at times of 40 min, 80 min, and 120 min from each beaker with the help of micropipette. This procedure was followed for all experiments.

2.3.3. Measurement of concentration

After 120 min of stirring, samples taken from each beaker were centrifuged at 3000 rpm for 15 minutes, to separate supernatant and coal fly ash. Then the final dye concentrations for the samples were obtained by measuring absorbance by using UV VIS Double Beam Spectrophotometer (Shimadzu 1800) at 650 nm wave length. Then the final concentration of methylene red dye in terms of mg/l or ppm was obtained from the absorbance data using standard calibration curve. The adsorption performance of the prepared coal fly ash was calculated using the following equation.

$$\%\text{MR removal} = \frac{Co-C1}{Co} \times 100$$

Where:

C_0: is initial concentration of methylene red (ppm)

C_1: is final concentration of methylene red (ppm)

After the equilibrium concentrations of methylene red dye was determined, the adsorption capacity, qe, was calculated as:

$$qe = \frac{Co-Ce}{m} \times V$$

Where:

Co and Ce are the initial and equilibrium dye concentrations in (mg/L) respectively, V is a known volume of methylene red solution (L), and m is a known mass of dry coal fly ash (g).

3. Results and discussion

3.1 Effect of Contact time on dye removal and adsorption capacity

For different contact time values the percentage removal of dye and adsorption capacity of coal fly ash was recorded. The effect of contact time on removal of methylene red and adsorption capacity of coal fly ash is shown in Fig. 1. From the figure, it can be seen that as contact time increased from 40 min to 120 min, the percentage removal of methylene red increased. The increment in percentage removal is rapid in initial stage and becomes slower later when it approaches equilibrium. The change in the rate of adsorption might be due to the fact that initially all the adsorbent sites are vacant and solute concentration gradient was very high.

Fig 1. Effects of contact time on percentage removal of methylene red.

The optimal contact time to attain equilibrium was experimentally found to be around 100 min. The adsorption capacity of coal fly ash changes slightly from the start of adsorption process. This might be because of the imbalance between dye concentration and adsorbent dose.

Fig.2 Effects of contact time on adsorbance capacity.

3.2. Effects of adsorbent dose on dye removal and adsorption capacity

The adsorbent dose was varied from 0.5 g to 1.5 g per 150 ml of methylene red solution. For different adsorbent dose values the percentage removal of dye and adsorption capacity of coal fly ash was analyzed. The effect of adsorbent dose on removal of methylene red and adsorption capacity of coal fly ash is shown in Fig. 3. In Fig.3 the percentage removal of dye increases with an increase in mass of adsorbent while the adsorption capacity of coal fly ash decreased. As the adsorbent dose increased from 0.5 g to 1.5g, the percentage removal of dye increased from 94.24 % to 98.39 % for contact time of 80 min. The increase of the percentage removal with the increasing adsorbent mass is due to the increase in the number of adsorbent particles with a larger number of active surface sites for the adsorption. The optimum mass of adsorbent and time of adsorption to attain maximum percentage removal was experimentally found to be 1.0 g and 120 min respectively.

Fig. 3 Effects of adsorbent dose on the percentage removal of dye.

On the other hand, as adsorbent dose increased from 0.5 g to 1.5 g adsorption capacity decreased from 7.07 mg/g to 2.46 mg/g at 25 mg/l of dye solution. This may be due to the existence of too low dye concentration for the available adsorbent (active sites).

Fig. 4. Effects of adsorbent dose on adsorbance capacity.

3.3 Effects of initial concentration on dye removal and adsorption capacity

The effect of initial concentration on percentage removal of methylene red and adsorption capacity of coal fly ash was recorded by varying initial dye concentration from 25 mg/l to 75 mg/l. From Fig. 5 it is shown that the percentage removal of dye and adsorption capacity of coal fly ash increased with increasing initial dye concentration. This is due to the increase in the driving force of the concentration gradient between the adsorbate in the bulk solution and the active sites. The active sites of coal fly ash would be surrounded by more dye compounds and the process of adsorption would be carried out more intensively.

Fig. 5 Effect of initial dye concentration on percent removal of dye

The adsorption capacity is rapidly increasing and does not seems to reach equilibrium. This again show the over dose of adsorbent compared to the available dye particles.

Fig. 6 Effect of initial dye concentration on adsorbance capacity

3.4. Adsorption Isotherm Models

The Langmuir and Freundlich adsorption models were used to study the methylene red adsorption behavior of coal fly ash.

3.4.1 Langmuir isotherm model

The arranged Langmuir equations is given by:

$$\frac{1}{qe} = \frac{1}{qm} + \frac{1}{qm \times KL \times Ce}$$

Where Ce is the equilibrium concentration of the dye solution (mg/l), qe is the amount of dye adsorbed per unit mass of adsorbent (mg/l), qm and KL are the Langmuir constants. Fig. 7 shows the linear plot of (1/qe) versus (1/Ce) suggesting the applicability of the Langmuir model.

Fig. 7 Langmuir model curve for coal fly ash

The values of constants (q_m and K_L) in the Langmuir model were calculated from the plot and are listed in table 1. The value of dimensionless equilibrium parameter R_L, used to express the essential characteristics of Langmuir isotherm, was found to be 0.0028 which is in the range of ($0<R_L<1$) confirming that the adsorption process is favorable for adsorption of methylene red on coal fly ash under the conditions used in this study.

3.4.2. Freundlich Isotherm model

The simplified Freundlich Isotherm equation given by: $\ln(qe)=\ln(Kf)+\frac{1}{n}\ln(Ce)$

Where, Kf and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity of the adsorbent, respectively. The linear plot of ln(qe) versus ln(Ce) is shown in Fig. 5. The values of Freundlich model constants Kf and 1/n calculated from the intercept ln(Kf) and the slope (1/n) of the plot are listed in Table 1.

The values of R^2 and R_L obtained from experimental work indicate that equilibrium data was best fitted to both the Langmuir and Freundlich isotherm models.

Table1. Calculated values of Langmuir and Freundlich model constants

4. Conclusion

The coal fly ash generated from coal based thermal power plant was used as low-cost and effective adsorbent for the removal of methylene red dye from an aqueous solution. Removal of methylene red dye was affected by operating parameters like adsorbent dose, initial dye concentration and contact time. It is found that, the percentage removal of dye increases by varying adsorbent dose, initial dye concentration and contact time to optimum condition. The optimum conditions of adsorption found from this study are 1 g of coal fly ash for 25 mg/L of Methyl red dye aqueous solution for 120 min of contact time at pH of 6.8. The results indicate that, coal fly ash is a good adsorbent for Methyl Red dye removal and follows both Langmuir and Freundlich isotherm models. Finally, the study demonstrated that, coal fly ash is a good adsorbent for Methyl Red removal and should be further studied for industrial applications.

References

Adib, M., Razi, M., Nur, M., & Mohd, A. (2017). Factor Affecting Textile Dye Removal Using Adsorbent From Activated Carbon : A Review, 6015, 1–17.

Bada, S. O., & Potgieter-vermaak, S. (2008). Evaluation and Treatment of Coal Fly Ash for Adsorption Application, (12), 37–48.

Carmen, Z., & Daniel, S. (2012). Textile Organic Dyes – Characteristics, Polluting Effects and Separation/Elimination Procedures from Industrial Effluents – A Critical Overview. Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update.

Durairaj, S., & Durairaj, S. (2012). International Journal of Pharmaceutical Research Colour Removal from Textile Industry Wastewater Using Low Cost, 3(1), 52–57.

Dwivedi, M. K., Jain, N., Sharma, P., & Alawa, C. (2015). Adsorption of Safranin from Wastewater Using Coal Fly Ash, 8(4), 27–35.

Farman, S., Shah, A., Aftab, A., & Soomro, N. (2015). Waste Water Treatment-Bed of Coal Fly Ash for Dyes and Pigments Industry, 16(2), 48–56.

Jain, N., Dwivedi, M. K., & Waskle, A. (2016). Adsorption of Methylene Blue Dye from Industrial Effluents Using Coal Fly Ash, 3(4).

Journal of Innovative Research in Science, E. and T. (2016). Removal of Dyes Using Leaves of Morinda Pubescens as a Low Cost Green Adsorbents. Innovative Research in Science, Engineering and Technology, 5(2), 1565–1571.

Journal of Innovative Research in Science, E. and T. (2017). Removal of Methylene Blue Dye from Waste Water Using Agro – Waste as Low Cost. Innovative Research in Science, Engineering and Technology, 6(3), 3426–3431.

Kanawade, S. M., & Gaikwad, R. W. (2011). Removal of Dyes from Dye Effluent by Using Sugarcane Bagasse Ash as an Adsorbent, 2(3), 2–6.

Kant, R. (2012). Textile dyeing industry an environmental hazard, 4(1), 22–26.

Kumar, A., Chaudhary, P., Verma, P., & Kumar, A. (2013). Adsorption of Reactive Red 194 Dye from Textile Effluent by Using Class F Fly Ash, 1(2), 111–116.

Maria, P. univ. dr. (2014). Autor: Prof. univ. dr. Maria VIŞA - 2014 –.

Mehta, M. J., & Chorawala, K. K. (2014). Adsorptive Removal Of Dye From Industrial Dye Effluents Using Low-Cost Adsorbents: A Review. Journal of Engineering Research and Applications Www.ijera.com ISSN, 4(5), 2248–962240.

Nadu, T. (2011). Dye removal from aqueous solution using low cost adsorbent, 1(7), 1492–1503.

Ramesh, K. S. B. S. T. (2013). Removal of dyes using agricultural waste as low-cost adsorbents : a review, 773–790.

Sareen, D., Garg, R., & Grover, N. (2014). A Study on Removal of Methylene blue dye from waste water by Adsorption Technique using fly ash briquette. International Journal of Engineering Research & Technology, 5(4), 610–613.

Shah, A. K., Ali, Z. M., Laghari, A. J., Farman, S., Shah, A., & Pollutants, W. (2013). Research and Reviews : Journal of Engineering and Technology Utilization of Fly Ash as Low-Cost Adsorbent for the Treatment of Industrial Dyes Effluents- A Comparative Study ., 2(1), 1–10.

Tahir, H., Sultan, M., Akhtar, N., Hameed, U., & Abid, T. (2012). Application of natural and modified sugar cane bagasse for the removal of dye from aqueous solution. Journal of Saudi Chemical Society.

Table1. Calculated values of Langmuir and Freundlich model constants

Langmuir Model			Freundlich Model		
qm	KL	R^2	Kf	n	R^2
22.22	3.027	0.9308	22.2	0.002	0.9799

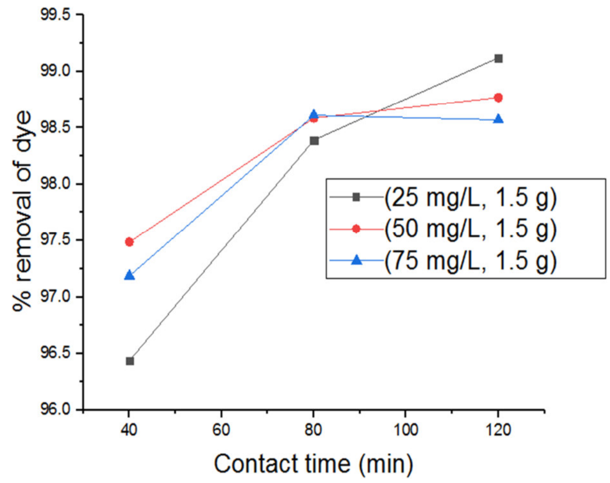

Fig.1. Effects of contact time on percentage removal of methylene red.

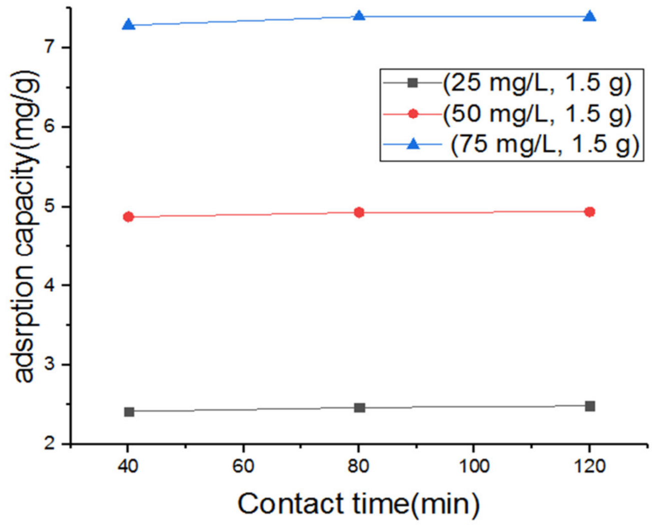

Fig.2. Effects of contact time on adsorbance capacity.

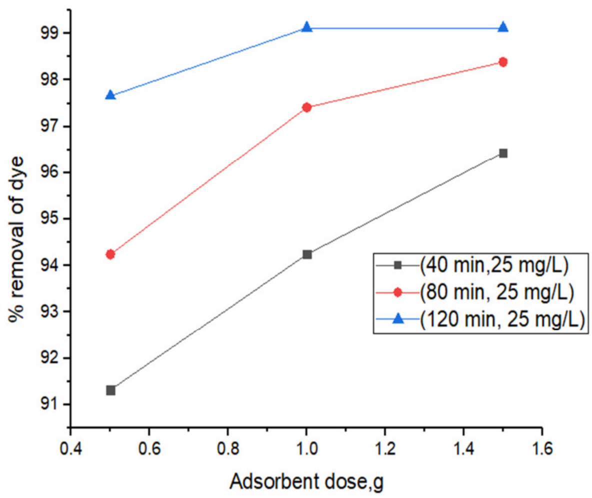

Fig. 3. Effects of adsorbent dose on the percentage removal of dye.

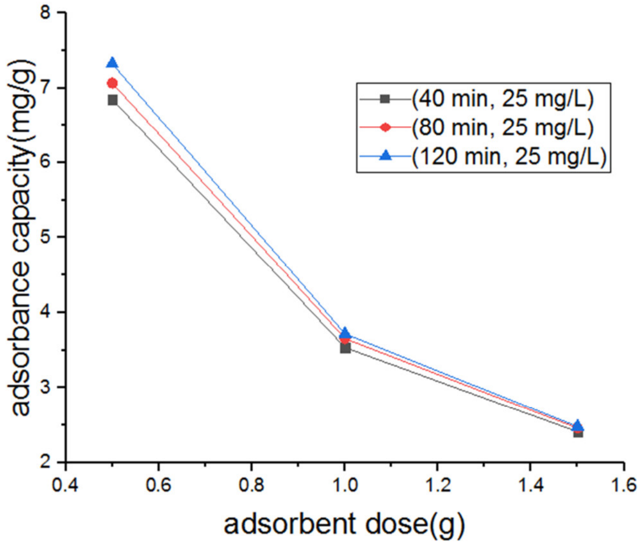

Fig. 4. Effects of adsorbent dose on adsorbance capacity.

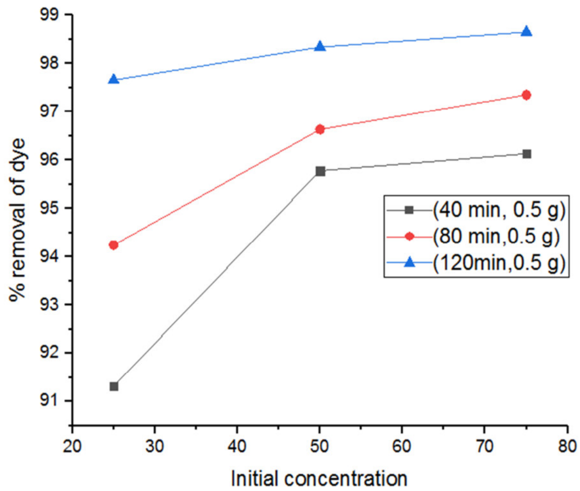

Fig. 5. Effect of initial dye concentration on percent removal of dye

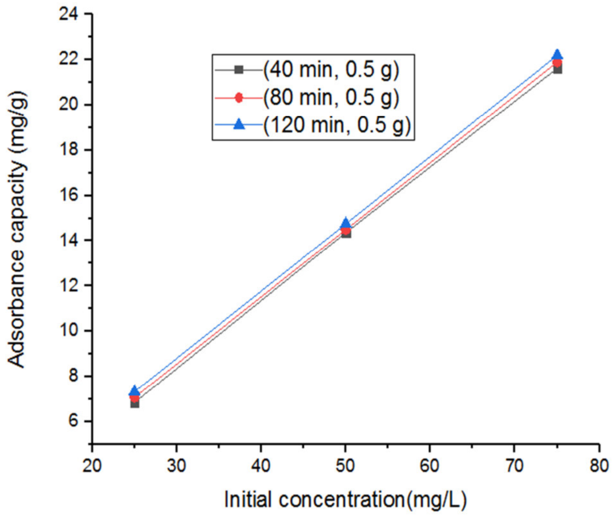

Fig. 6. Effect of initial dye concentration on adsorbance capacity

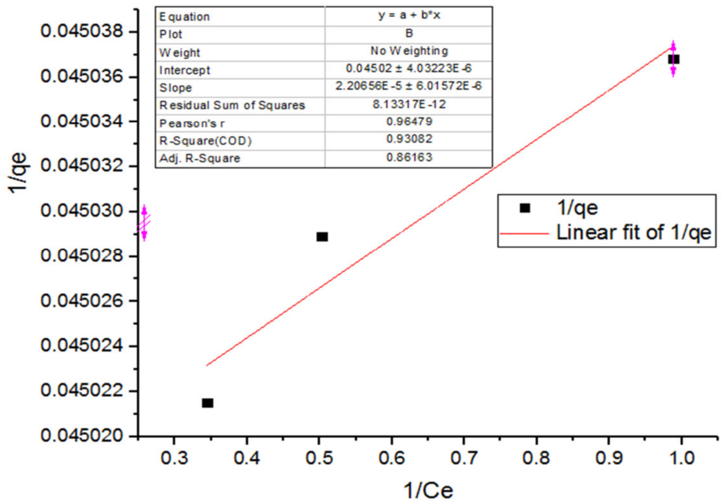

Fig. 7. Langmuir model curve for coal fly ash adsorption.

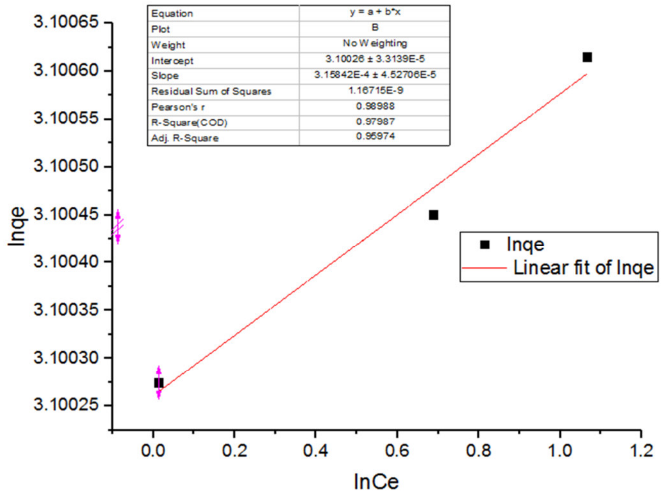

Fig. 8. Freundlich model curve for coal fly ash adsorption.