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Adsorption studies on the reduction of COD and color from textile dyeing effluent using wheat husk adsorbent

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This study is an attempt to remove the organic compound present in textile dyeing effluent in form of color and chemical oxygen demand (COD) from treated textile dyeing effluent (TDE) using adsorption. For this work, wheat husk adsorbent (WHA) is successfully prepared at laboratory scale by carbonization of wheat husk by a double stage carbonization process include $ZnCl_2$ activation. The experimental work performed to analyze the influence of different operating parameters like adsorbent dose, pH, contact time between adsorbate and adsorbent, particle size, and temperature on COD and color reduction. The results confirmed that maximum color and COD reduction of 90.01% and 86.1%, respectively were achieved at optimum conditions (i.e. at pH 4, temperature 25°C and WHA dose of 2.5 g/dm^3). The kinetic studies have been performed on the basis of varying organic concentrations using pseudo-first order and pseudo-second-order kinetics. Furthermore, pseudo-second order (R^2 = 0.99) is found to fit better than pseudo-first order (R^2 = 0.97) in term of regression coefficient's values as evident from the kinetic studies. For the suitability of data observation, adsorption models such as Freundlich and Langmuir were applied for equilibrium studies. Both models were found suitable in this study with R^2 = 0.99.

Keywords: Chemical oxygen demand, color, adsorption isotherm, kinetic models, wheat husk, $ZnCl_2$ activation.

Introduction

Textile industries are one of the most employable sector therefore it is one of the important segments of world economy. However, large amount of fresh water is used during the process which causes large amount of wastewater generated. This wastewater contains several impurities therefore its proper treatment is required. Apart from this if this wastewater is directly discharge in any water source like rivers and canals then it can pollute their aquatic system as well it is responsible for several diseases leads to carcinogenic effects.

The fabric preparation is completed in two processes namely dyeing and wet process. Wet process involves several stages including dyeing, bleaching etc. It is well known fact that dyeing is a common step during the wet process activity. During the dyeing process, large quantity of raw water is used consequently large amount of wastewater is generates in this section. Wastewater discharge from dyeing unit is called textile dyeing effluent (TDE). Textile industries uses different type of dyes to get desired color during textile process, therefore TDE contains large amount of color as well as high demand of chemical oxygen (COD). Furthermore, it also contains dyes residues which are small particle of dyes and also different types of chemicals. Therefore, it cannot be discharge directly in any pure stream without its proper treatment. Apart from this, discharge quality of the treated industrial effluent is also monitored by Indian regulation agencies like the Central Pollution Control Board (CPCB) of India, for discharge of TDE into any water receiving media[1].

Now a day so many technologies are used to treat textile dyeing effluent such as coagulation, filtration, ozonation, thermolysis, membrane separation, advanced oxidation process, wet air oxidation, adsorption etc. These treatment technologies have several limitation includes large amount of sludge generation, high operating cost etc. Besides this adsorption is a potential alternative to treat TDE, due to its high organic

Table 1. Comparison of percentage of COD and color removal by various laboratory made adsorbents

Adsorbent types	Type of wastewater	COD removal (%)	Color removal %	Ref.
Wheat husk adsorbent	Textile dyeing effluent	86.1	91.01	This work
Powdered activated carbon	Textile wastewater	78	86	2
Bamboo-based activated carbon	Textile wastewater	75	91	3
Bagasse fly ash	Pulp and paper wastewaters	50	55	4
Coconut shell carbon	Industry mixed wastewater	46–71	–	5
Rise husk carbon	Industrial mixed wastewater	45–73	–	6
Adsorbent from fertilizer waste	Industrial wastewater	>50	–	7

removal efficiency, easy installation, simple operation, easy to use and environmental friendliness. The detailed literature review of adsorption treated waste water is presented in Table 1. This table also presents a comparison study with present work.

There are several types of agricultural waste materials such as different plant leaves (Neem), roots of plant, coal, wood and coconut shell etc. are used for the production of adsorbent (activated carbon). In addition, recently groundnut shell is also used as adsorbent[6]. India is the large producer as well large consumer of wheat in the world, therefore large amount of wheat husk generated during the separation of wheat from its original crops hence there is a huge potential in the utilization of wheat husk. Wheat husk is agriculture waste which contains mostly carbon and fiber and creats a disposal problem. Furthermore, wheat husk is burn in open atmosphere by farmers which causes serious environmental problem. Therefore, it is necessary to develop a valuable product by wheat husk such as activated carbon. Wheat husk contains greater amount of non-carbon constituents as compared with coal hence the chances of retaining functional groups is better[7]. Consequently, activated carbon prepared by wheat husk has ability to provide better reduction of pollutants from waste water as compared with standard adsorbent (traditional activated carbon which prepared by coal).

The aim of this work is to utilize agricultural waste as an adsorbent (activated carbon) from wheat husk and to investigate organic adsorption capacity of it, in term of color and COD reduction from TDE. Different operating parameters (pH, time of contact, dose of adsorbent and adsorbent size) were examined to find out the efficiency of wheat husk as a commercial adsorbent. Furthermore, the adsorption isotherms are also tested.

Experimental

TDE and its characterization:

The TDE is first treated by electro coagulation and it is reported in our previous work[8]. To maintain parameter of electro coagulated TDE, the collected waste water is kept at 4°C in a deep freezer. Wheat husk adsorbent (WHA) is used as potential adsorbent. The treated effluent is examined by various parameters including COD, color, hardness etc. by well prescribed method (APHA)[9]. The characteristic of the treated and original textile dyeing effluent is presented in Table 2.

Table 2. Typical composition of EC treated TDE and adsorption treated TDE

Parameters	EC Treated Textile dying effluent	Adsorption of treated TDE at optimum condition
COD	1153.8	161.5
TDS	1012	512
TSS	2613	894
TS	3625	1406
Chloride	59	28
Phosphate	7	3
Total hardness	1418	300
Sulphate	–	–
pH	6.0	4
Color	Light brown	Lighter brown transparent
Absorbance at λ = 475 nm	0.225	0.0225
Color (PCU)	145.8	14.58

All value in mg/dm^3 except pH and color.

Adsorbent preparation in laboratory scale:

The properly washed wheat husk is converted in charcoal in a furnace. Agriculture waste is taken in a closed SS (stainless steel) container and heated at 300°C for 0.25 h in a furnace followed by chemical activation with the help of 50% $ZnCl_2$ solution for 20 h at ratio 1.70 (zinc chloride/char) then allowed to dry at 100°C. Additionally, at 600°C the dried char (saturated with Zn) was heated for 20 min. For the safety point of view, activated carbon is treated with hydrochloric acid (1:1) for the removal of saturated salts and distilled water washing is done for the removal of chlorides[10].

Adsorption and kinetic analysis:

The batch experiments are performed; in which 50 ml sample is taken in conical flask (250 ml) with 0.1 g of wheat husk adsorbent and placed it in a thermo stated shaker (120 rpm). 1 *N* solution of HCl/NaOH was used to maintained the pH of effluent (TDE). The influence of different parameters like initial pH of TDE, organic load in term of COD concentration, dose of adsorbent, time of contact, temperature and particle size on the adsorption process are also studied. For the approval, number of experiments was repeated whenever required.

The amount of COD reduced/weight of adsorbent, q_e (mg/g) was obtained by eq. (1).

$$q_e = \frac{V(C_o - C_e)}{W \times 1000} \tag{1}$$

where, V = Volume of TDE in liter

C_o = Concentration of COD at time t_0 (mg/L)

C_e = Concentrations of COD at time t_t (mg/L)

W = weight (g) of adsorbent.

Steps of adsorption equilibrium and kinetic studies during adsorption:

Equilibrium studies are performed in batch experiment at COD concentration range 300–1500 mg/L in a conical flask of 250 ml arranged in series. For this experiment 50 mL effluent was taken in each flask and maintaining required pH and temperature. Further, calculated amount of WHA was mixed in each conical flask and was kept in shaker (isothermal) at 120 rpm to obtain equilibrium. After fixed time interval, the samples were withdrawn to find COD in TDE. It is observed that the equilibrium condition was achieved at the contact time of 360 min. At different temperature range (20 to 40°C), the effect on the adsorption process is also studied.

Above described technique is used for kinetic tests. To explain the adsorption kinetic studies different experiment are performed for four different initial COD concentrations at pH 4 and at working room temperature of 25°C.

Results and discussion

Characterization of adsorbents:

To analyze the characteristics of a material, X-ray diffraction (XRD) is an important technique to find whether the material is crystalline or amorphous. In addition, XRD is also useful to determine quality of product. The prepared carbon was characterized by XRD using 2θ values ranges from 20° to 80°. The XRD pattern of prepared wheat husk adsorbent is presented in Fig. 1. It can be seen from the Fig. 1 that successive peaks occurs at 28° which shown high purity of the WHA and product is crystalline in nature.

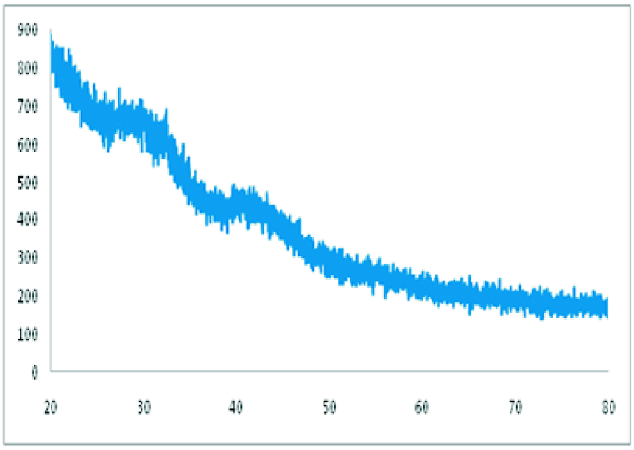

Fig. 1. X-Ray diffraction (XRD) of WHA adsorbent.

To understand morphological structure of prepared material SEM study is also done and shown in Fig. 2a and 2b. It can be observe from Fig. 2a that the outer structure of the adsorbent is not smooth (rough surface) and porous structures are existing of different sizes.

Apart from this, Fig. 2b represents the SEM image of WHA after the treatment of TDE effluent which shows the smooth structure of material. This may be due to the presence of inside cavities in the porous structure which are covered by organics. It is also observed that the pores on the walls of the WHA have higher surface area along with high adsorption capacity.

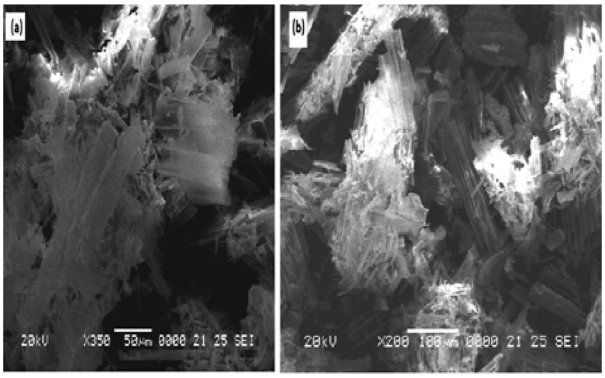

Fig. 2. SEM images of: (a) pre-treated WHA and (b) post-treated WHA.

Adsorption studies:

Effect of initial pH:

Activated carbon is known to contain positive charge or negative charge on their surface hence it show dual nature which highly depends on pH of the solution. In addition adsorbent also contain several functional groups. The adsorptions of organics contents are oriented on the ionic state and types of present functional groups. Therefore, how pH influence the COD reduction is examined at different pH range (2–10) with ambient temperature of 25°C. Fig. 3 showed the effect of pH on COD reduction of TDE. Fig. 3 demonstrated that better COD removal is achieved at acidic pH and maximum adsorption of organic content is found at pH 4. Further, with increase in pH, COD removal efficiency decreases and only marginal change are observed. At pH 4, the removal of COD 86.17% and color was 90.01% which reduced to 50.5% and 61.85% at pH 10. In TDE different type of organics are present which have their own functional groups which posses net negative charge. Adsorbent have positive surface charge consequently the value of Van der Walls forces increases which promotes adsorption of organic material. Furthermore, the large number of hydrogen ions is generated in acidic range, which is responsible to neutralize the negatively charged adsorbent surface[11]. Hence, further work is done at pH 4 considering it optimal pH for organics (COD) adsorption on prepared WHA. It is reported by Chowdhury *et al.*[12] that pH was highly influenced during adsorption of basic green 4 dye by adsorbent prepared by leaf of *Ananas comosus* and maximum removal is achieved at pH 10. Similar type of experiment is performed by Dawood and Sen[13] for removal of Congo red from waste water with the help of pine cone as an adsorbent and reported that pH 3.5 gives maximum dye removal.

Effect of WHA dose during adsorption:

The dose of adsorbent is one of the surrogate parameter for removal of COD from the TDE. Therefore, experiments were performed in different adsorbent doses (1–3 g/dm^3), and COD reduction during these experiments are presented in Fig. 4. It is clear from the Fig. 4 that COD removal efficiency was noted in increasing order from 50.81% to 90.22% and color removal efficiency also followed the pattern of COD reduction which increased from 51.15% to 97.8% with varying dose of adsorbent from 1 g/L to 3 g/L. This is attributed to

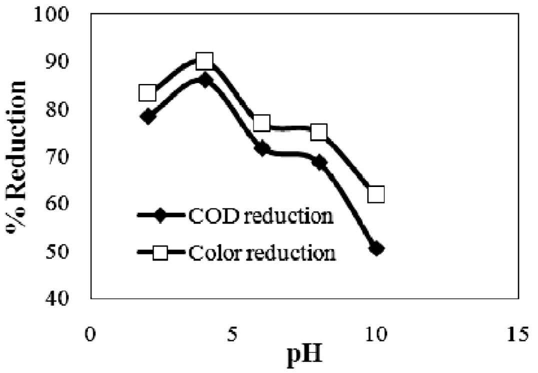

Fig. 3. Effect of pH on COD and color reduction at 25°C and pH 4 and 25°C.

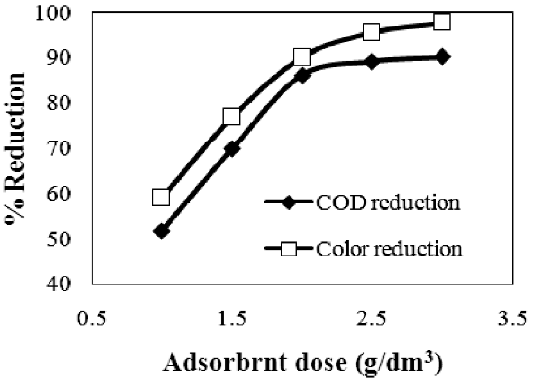

Fig. 4. Effect of adsorbent dose on COD and color reduction at WHA dose 2.5 g/dm^3.

the reality that more surface area is available when the amount of adsorbent increases, for the same order for adsorption. However, upto a certain limit the reduction of both color and COD insreases after then it starts decreasing. Srivastava *et al.*[14] also performed this type of work and used bagasse fly ash and poly aluminium chloride for the treatment effluent which was collected from the paper mill.

Effect of particle size during adsorption:

The reduction of COD and color by adsorption are also performed with different size of adsorbent (30 to 130 μM) where adsorbent dose is kept constant (2.5 g/dm^3). The results of COD reduction versus particle size are presented in Fig. 5. From the Fig. 5, it can observe that the capacity of adsorption increases with decrease in particle size of WHA. COD removal efficiency increases from 12.44% to 88.17% and color 15.18% to 93.8% with decrease in WHA adsorbent size (130 to 20 μM). This may be due to the fact that low particle size had offered more amount of surface area hence high COD and color reduction was observed with low particle size[14].

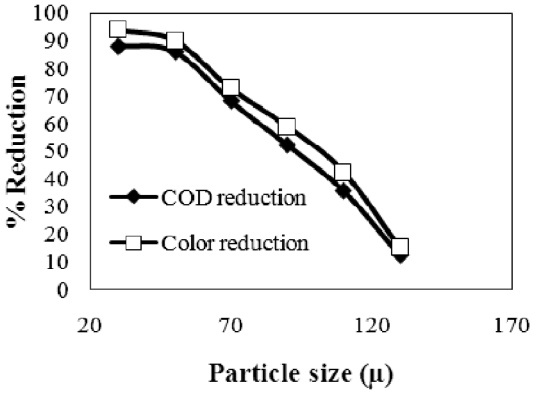

Fig. 5. Effect of particle size on COD and color reduction at pH 3.5 and adsorbent dose 2.5 g/dm^3.

Effect of temperature during adsorption:

During the adsorption process, temperature is again the most important operating parameter. Therefore, the effect of temperature during adsorption process is studied at varying temperatures range (20–45°C) and results are presented in Fig. 6. At 20°C COD and color removal were achieved to 80.1% and 83.8% which continue to increase up to 92.9% and 94.6% at 45°C. This may be due to high temperature which is responsible for increasing diffusion rate of adsorbate molecules. In addition, fluctuation in working temperature can highly influenced the particular adsorbate to obtain equilibrium capacity. This work shows that adsorption process is endothermic in nature.

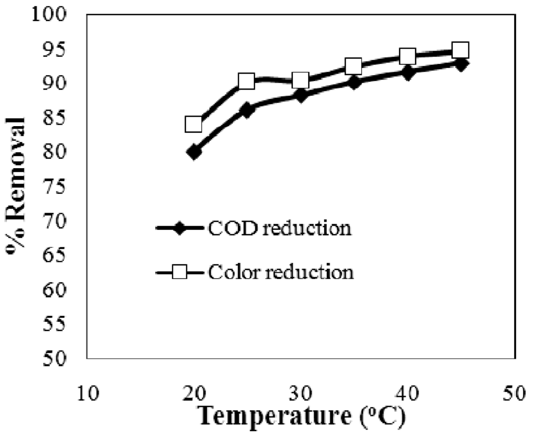

Fig. 6. Effect of temperature on COD and color reduction at pH 3.5 and 25°C.

Effect of contact time and initial concentration during adsorption:

Influenced of the contact time during adsorption process in terms of COD adsorption is presented in Fig. 7. To investigate this effect, experiments are performed by using WHA at different concentration range of COD (300–1500 mg/dm^3) at pH 4 and at ambient temperature. It is reflected from Fig.

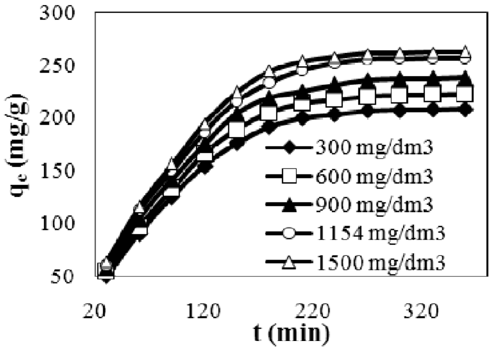

Fig. 7. Effect of contact time on COD reduction at initial feed concentration, pH 4 and 25°C.

7, when the contact time increases the COD adsorption rate also increases in same order. It is also observed that the uptake of organics is high in initial 180 min; then after adsorption rate decreased and ultimately achieved equilibrium. Furthermore, at the contact time upto 210 min, the saturation point was observed. In the initial 180 min, COD adsorption is fast due to presence of uncovered surface and availability of active sites on the WHA.

Adsorption kinetics:

Adsorption kinetics is a way to understand the mechanism of the various reactions. Kinetic studies are done by using two kinetic model pseudo-first order and pseudo-second order. Both models are well applicable for the conformation of experimental data within the model predicted values. However, correlation coefficient (R^2) is very useful to check the validity of the model. The values of R^2 are able to describe the COD adsorption kinetics.

For solid-liquid systems, the pseudo-first order equation can be given as:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (2)$$

where, organics adsorbed (mg/g adsorbent) with time t is represented by q_t and q_e, where system got equilibrium, k_1 is a constant which included with adsorption rate (min^{-1}) also called rate constant. Organic adsorption in term of COD reduction is presented in Fig. 8 which shows linear form of the pseudo-first order model. The slope of plots of log ($q_e - q_t$) versus t gives the rate constant k_1 which is 0.007. For the pseudo-first order kinetic model, R^2 is found in the range of 0.96–0.97 which show data is not obtained in linear form therefore it cannot be well explained by this model.

Above description demonstrated that the expected results is not obtainable by pseudo-first order equation, hence the pseudo-second order adsorption kinetic can be tested to get closer result which is given as[15]:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \qquad (3)$$

where, at equilibrium and time t the sorption capacity of organics in term of COD is given by q_e and q_t (mg/g), rate of adsorption [mg/(g.min)]. Is represented by constant, k_2.

The eq. (3) may be simplified as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \qquad (4)$$

where, the initial adsorption rate, h [mg/ (g.min)] is given as:

$$h = k_2 q_e^2 \qquad (5)$$

The graph between t/q_t versus t for eq. (5) is presented in Fig. 9. The value of k_2 found in the range of 0.018–0.022 and the correlation coefficient (R^2) value 0.99 is observed for pseudo-second order kinetic model which indicates current adsorption system followed the second order kinetic model.

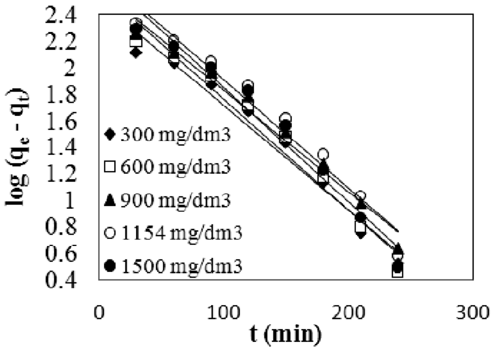

Fig. 8. Lagergren first order plot for COD reduction for different initial feed concentration, pH 4 and 25°C.

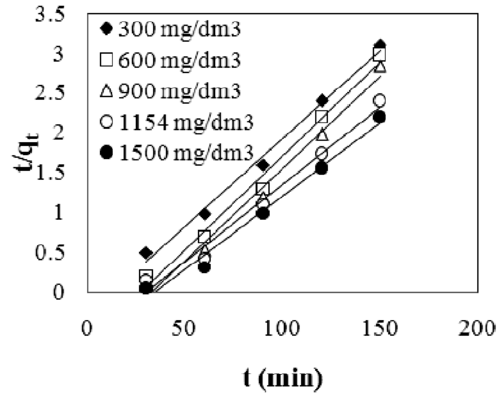

Fig. 9. Pseudo-second order kinetic plot for COD reduction at different temperatures and pH 4.

Analysis of adsorption isotherm models:

Adsorption isotherm models are effectively used to explain and understand the purpose of the fraction of sorbet molecules that are divided between solid and liquid phases at equilibrium. Therefore, two important isotherm models namely; Langmuir and Freundlich were undertaken. The isotherm proposed by Langmuir is presented as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (6)$$

where, equilibrium concentration (mg/L) of organics in term of COD is represented by C_e, amount of organics adsorbed in term COD (mg/g) at equilibrium by q_e, theoretical adsorption capacity of monolayer in (mg/g) is by q_m, and K_L is a constant (L/mg).

The graph between C_e/q_e against C_e is presented in Fig. 10 in term of COD adsorption. This graphical presentation indicates Langmuir adsorption isotherm is validated within experimental data hence surface of adsorbent is well suitable with adsorbate for the phenomenon of monolayer formation. In addition, Langmuir constant K_L was found 0.004 and R^2 was found 0.99.

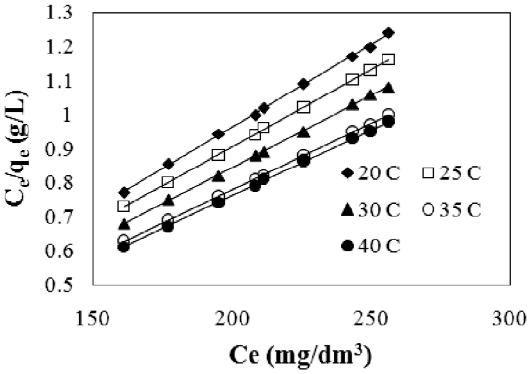

Fig. 10. Langmuir adsorption isotherms for COD at various initial feed concentration, pH 3.5 and 25°C.

In this work, Freundlich isotherm is also used to check its validity. For these initial COD concentrations of effluent is varied at constant adsorbent mass. The equilibrium time was considered 210 min is for sorption experiments. The Freundlich isotherm equation can be expressed as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad (7)$$

where, K_f (mg/g) and $1/n$ (g/L) are Freundlich adsorption constants.

The plot between ln q_e against ln C_e shows straight lines as given in Fig. 11. The value of K_F was found 1.07 and the values R^2 are 0.99 which indicates that the Freundlich isotherm model was suitable with the experimental data.

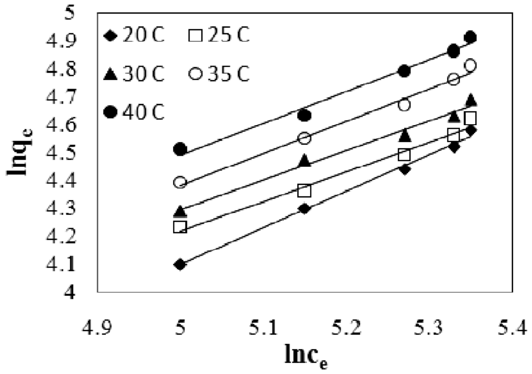

Fig. 11. Freundlich adsorption isotherm for COD reduction at different temperatures and pH 4.

Conclusion

WHA is successfully prepared from wheat husk carbonization followed by $ZnCl_2$ activation, which provided good result in term of COD removal from TDE. The availability of wheat husk in India is easy hence it can be used to prepare an adsorbent for removal of organics. Work demonstrates that COD and color removal is highly depend on TDE, effluent pH and its initial feed concentration. 86.17% COD removal for initial COD = 1154 mg/dm^3 and 96.2% color removal for initial color = 254 PCU were achieved at pH 4, temperature 25°C and WHA dose of 2.5 g/dm^3. The % COD reduction is increased with decrease in size of WHA particle and decreases with decrease in WHA dose. The kinetics of COD is validated for pseudo-second order with $R^2 \approx 0.99$. Frendulich isotherm model fitted poor as compared to Langmuir adsorption isotherm model in term of temperature range studied. COD adsorption on WHA was observed endothermic because the values of K_L and q_m were large at high temperatures.

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