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Efficient utilization of bio-energy process residue for removal of Drimarine Yellow HF-3GL dye from aqueous solution

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ABSTRACT

Bio-energy is an emerging field to address the energy crisis. The biomaterials used in bio-energy production processes undergo various chemical/physical/biological treatments which lead to the activation of biomass. The exploitation of residual biomass of bio-energy processes for wastewater treatment is an attractive option. In this work, the de-oiled/residual biomass of an insect species; *Trogoderma granarium* (khapra beetle) which was neither previously exploited for biofuel production nor for wastewater treatment was tested for the adsorptive removal of Drimarine Yellow HF-3GL dye from aqueous solution. The study was designed in batch mode, and important influencing parameters have been optimized including pH, contact time, biomass dosage, temperature and initial dye concentration. The residual insect biomass depicted maximum adsorption capacity (481.9 mg/g) by keeping solution pH 2 and temperature at 30°C. Adsorption of Drimarine Yellow HF-3GL dye onto insect residual biomass was found to be a quick process and equilibrium was attained within 15 min. The adsorption mechanism was investigated by applying different equilibrium models. Thermodynamic study was also conducted to check out the feasibility of process. Different kinetic models have been applied on experimental results and pseudo-second-order kinetic model was found to be best fitted on the experimental results. The biomass was characterized by Fourier transform infrared spectrometer analysis, scanning electron microscope analysis and point of zero charge determination (pH_{pzc}). The study results indicated that *Trogoderma granarium* de-oiled biomass has good adsorption potential and bio-energy process residues can be an attractive option for reducing the water pollution.

Keywords: *Trogoderma granarium* (khapra beetle); Adsorption; Equilibrium study; Kinetic study; Thermodynamic study

1. Introduction

There are two major challenges which the people of this planet are currently facing: energy crisis and environmental pollution [1]. The requirements of transportation fuel are mostly fulfilled by fossil fuels globally [2]. The alternative energy resources have become an important strategic direction of global energy structure. This is majorly due to continuous consumption and depletion of fossil fuel reserves [3]. Researchers are attempting to explore novel biomaterials with good potential for biofuel production. The potential of insects for biofuels production is an emerging field. *Trogoderma granarium* (khapra beetle) is a serious pest of stored grains and a lot of studies have been reported on the

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control measures of *Trogoderma granarium* with food safety point of view [4–9]. But it is a very potential option for biofuel production with 53% fat content in its body. No study has yet been conducted to explore the potential of this pest for bio-energy production. Insects are most diverse group of organisms but no literature has been available which show the exploitation of insect biomass for wastewater treatment.

Water pollution is a serious concern for everyone because the availability of clean water resources is limited [10,11]. There is an increase in daily water consumption requirements due to rapid population growth. Faisalabad is the major textile city of Pakistan with large number of textile industries. Textile sector of Pakistan has major contribution in the economy of the country but along with this, it is also a major contributor of water pollution. Most of the textile industries are releasing their effluents without any treatment which contains high amount of synthetic dyes [12]. This colored effluent is creating aesthetic and health problems for human beings and aquatic organisms. The colored wastewater blocks the sunlight penetration into water which results in the decrease of photosynthesis by aquatic plant which ultimately results in disturbance of aquatic life.

Different techniques are adopted and tested by different scientists to suggest efficient and cost-effective way for reducing the water pollution. Adsorption has been found efficient for the treatment of wastewaters. The functional groups on the surface of biomass attach the contaminant molecules on its surface and decolorize the water. The exploitation of waste materials for this purpose is most suggested and attractive option. During bio-energy production processes, the biomaterials undergo various chemical, physical and biological treatments which lead to the activation of biomass. The left over biomass after biofuel production process can be exploited as a good adsorbent for wastewater treatment.

In adsorption process, the recovery and reuse of biomass is an important step for scale up applications. Immobilization of biomass on a suitable supporting matrix has also proved beneficial for scale up studies of wastewater treatment process [13,14]. Moreover the immobilization of biomass also helps in the solid–liquid separation and minimizes the biomass clogging issues in continuous flow systems. Different polymeric materials can be used for the immobilization of biomass, for example, alginate, chitosan, chitin and cellulose derivatives, etc. [15,16]. The present study was designed to evaluate the adsorption potential of *Trogoderma granarium* de-oiled biomass in free and immobilized forms for the removal of Drimarine Yellow HF-3GL dye from aqueous solution. Important influencing parameters have been optimized during batch mode experimentation.

2. Materials and methods

2.1. Preparation of biomass

The *Trogoderma granarium* larvae were obtained from Insect biofuel Lab, Punjab Bioenergy Institute, University of Agriculture, Faisalabad. The insect larvae were put into hot boiling water for instant death. The dead insect larvae were oven dried at 103°C for 24 h. Dried biomass was subjected to fat extraction in Soxhlet extractor using *n*-hexane at 60°C. The extracted fat was tested for biofuel production. The de-oiled biomass left after fat extraction was washed twice with distilled water and dried in oven at 103°C for 24 h. The dried biomass was ground and sieved to 300 μm mesh size by using sieve shaker (OCT-DIGITAL 4527-01, Endecotts Ltd., London, England).

2.2. Surface modification of biomass

In surface modifications, 1 g of *Trogoderma granarium* de-oiled biomass was treated with 5% solution of HCl, H_2SO_4 and NaOH. The chemical treatment was carried out in orbital shaker at 30°C and 120 rpm shaking speed for 1 h. Then, the modified biomass was washed with double-distilled water and filtered. The modified biomass was dried in oven at 103°C for 24 h and grounded for experimental use [17].

2.3. Immobilization of biomass

Biomass immobilization is an important step in wastewater treatment process because immobilized biomass helps in easy separation of adsorbent from the solution after completion of process. In the current study, sodium alginate was used to immobilize the adsorbent and the method used for immobilization of biomass was as reported previously by Bayramoglu et al. [16]. Brief description of this method is that in the first step, sodium alginate (2.0 g) was dissolved in 100 mL of water by heating and then the solution was cooled down. Insect de-oiled biomass (1 g/100 mL) was added to above mixture and mixed until to form a homogeneous mixture. Then the mixture was dropped into a solution of 0.1 M $CaCl_2$ to form uniform beads of immobilized biomass and finally the beads were washed with distilled water and stored at 4°C in 0.05 M $CaCl_2$ solution.

2.4. Preparation of aqueous dye solution

Drimarine Yellow HF-3GL dye was obtained from Clariant Pakistan Limited, Faisalabad, Pakistan. For the experimental work, stock solution 1,000 mg/L strength was prepared and the experimental solutions of different concentration were made by further dilutions. Drimarine Yellow HF-3GL dye was anionic in nature and its λ_{max} was 429 nm.

2.5. Batch experimental program

The batch mode study was conducted to optimize important influencing parameters which include pH, contact time, biomass dosage, initial dye concentration and temperature. The experiments were conducted with free and immobilized form of biomass in order to compare the adsorption potential of biomass in both of these forms. The experiments were conducted in 250 mL conical flasks containing 50 mL of dye solution of known pH, dye concentration and biomass dose and were shaken in orbital shaking incubator (SI Series, Sheldon Manufacturing Inc., USA) at 120 rpm shaking speed. Classical approach was adopted in this study in which one parameter is optimized at a time by keeping all other variables constant. Blank solutions were run under same conditions except the addition of biomass. pH of the solution was adjusted using 0.1 M HCl and NaOH solutions. All the experiments were performed in triplicate and reported values are

mean ± SD. After certain time, the samples were taken out and centrifugation was performed at 5,000 rpm for 20 min and concentration of remaining dye solution was determined by using UV–Vis spectrophotometer (Schimadzu, Japan).

The amount of dye adsorbed, q_e (mg/g), was calculated using the following relationship:

$$q_e = \frac{(C_o - C_e)v}{W} \quad (1)$$

where C_o is the initial dye concentration (mg/L), C_e is the equilibrium dye concentration (mg/L), V is the volume of the solution (L) and W is the mass of the biosorbent (g).

2.6. Kinetic study

For the kinetic study of adsorption process, the experimental data obtained from the optimization of contact time parameter was used. The contact time was optimized by using two different biomass dosages (0.1 and 0.05 g). The flasks were agitated for various time intervals (0–240 min) on an orbital shaker at 120 rpm under constant temperature (30°C). The samples were taken at different time intervals, centrifuged and analyzed for remaining dye concentrations as described before. The kinetic data were analyzed using pseudo-first order [18], pseudo-second order [19] and intra-particle diffusion [20] kinetic models.

2.7. Equilibrium study

For the equilibrium study, the experimental data obtained from the optimization of initial dye concentration experiment were used. This experiment was conducted by using different initial dye concentrations (10–1,000 mg/L) by dilution method. The experiments were carried out by taking known amount of *Trogoderma granarium* de-oiled biomass. The shaking speed was set at 120 rpm keeping temperature constant (30°C). The most commonly employed adsorption isotherm models were applied on the experimental data including Langmuir [21], Freundlich [22], Temkin [23], Harkins–Jura isotherm model [24] and Dubinin–Radushkevich (D–R) adsorption isotherm model [25].

2.8. Thermodynamic study

The effect of temperature on the removal of dye by using insect de-oiled biomass was investigated by varying the reaction temperature from 303 to 343 K. On the basis of experimental results, different thermodynamic parameters such as enthalpy changes (ΔH), entropy changes (ΔS) and Gibbs free energy changes (ΔG) were determined.

2.9. Characterization of biomass

The chemical characteristics of insect de-oiled free and immobilized forms of biomass were analyzed and interpreted by Fourier transform infrared spectrometer (FT-IR) with the samples prepared as KBr discs.

The point of zero charge (pH_{pzc}) was determined by solid addition method [26]. A series of 0.1 M KNO_3 solutions (50 mL each) were prepared and their pH was adjusted in the range of 1.0 to 12.0 by addition of 0.1 N HCl and NaOH. To each solution, 0.1 g of biosorbent was added and the suspensions were shaked manually and solution was kept for a period of 48 h with intermittent manual shaking. The final pH of the solution was recorded and difference between initial and final pH (ΔpH) (Y-axis) was plotted against initial pH (X-axis). The point of intersection of this curve yielded point of zero charge.

The surface structure of *Trogoderma granarium* de-oiled biomass was analyzed by JMT 300 scanning electron microscope (SEM; JEOL, USA).

2.10. Desorption study

Sorption procedure was carried out by adding 0.1 g of biosorbent in 50 mg/L of dye solution at optimized pH and temperature for 3 h. The amount of dye sorbed (mg/g) was calculated. Then filtered the dye solution and dried the dye loaded biosorbent in oven at 60°C and studied desorption process by shaking the dried biomass with different concentrations of NaOH and HCl ranging from 0.2% to 1.0%. The amount of dye desorbed (mg/g) was calculated. The % desorption can be estimated by using the following equation:

$$\text{Desorption}(\%) = \frac{\left[\text{Amount of dye desorbed}\left(\text{mg.g}^{-1}\right)\right]}{\left[\text{Amount of dye sorbed}\left(\text{mg.g}^{-1}\right)\right]} \times 100 \quad (2)$$

3. Results and discussion

3.1. Fat extraction from Trogoderma granarium larvae

The fat extraction was carried out in Soxhlet apparatus using *n*-Hexane as solvent. The extraction was done at 60°C. The complete fat extraction was achieved in almost 90 min. The total fat content from *Trogoderma granarium* dried dead insect larvae was 53% which shows very high fat content as compared with fat contents in other insects reported by different researchers [27]. The fat content in the insect body is different in its different developmental stages. The larval stage was selected for the estimation of fat contents because some researchers have reported that the maximum fat content in insect body is higher in its larval and pupal stages [28]. The high fat content and shorter fat extraction time (90 min) of the *Trogoderma granarium* makes it a very potential and economical option for biofuel production.

3.2. Surface modification of Trogoderma granarium de-oiled insect biomass

The biomass of *Trogoderma granarium* left after fat extraction was utilized for the treatment of textile effluents. An experiment was conducted to check whether the de-oiled biomass needs some more surface modification in order to enhance its adsorption potential or not. For this purpose, the de-oiled biomass was treated with acids (HCl and H_2SO_4) and alkali (NaOH). Usually, the acid treatment results in remarkable enhancement of adsorption capacity of biomass [29]. Acid treatment results in the removal of impurities from the surface of biomass which leads to enhanced

surface area and opening of binding sites [30]. The treated biomasses were tested for the removal of Drimarine Yellow HF-3GL dye. The experimental results indicated that the treatment of de-oiled *Trogoderma granarium* biomass with acids and alkali does not enhance its adsorption potential. 20.8 mg/g was the adsorption capacity by untreated de-oiled biomass. After treatment with HCl, H_2SO_4 and NaOH, the adsorption capacity was found to be 21.1, 20.6 and 17.2 mg/g, respectively. These results clearly depict that after pretreatment with weak acidic and alkali solution, there is no remarkable change in the adsorption capacity of biomass. This might be due to the fact that the fat extraction process itself acts as a surface modification step for the insect larvae biomass. The insect biomass remains in contact with *n*-hexane for 90 min at 60°C which results in opening of all the binding sites present on the surface of biomass. All the fat content present in the insect biomass has been removed due to its solubility into organic solvent (*n*-hexane). The biomass active sites become exposed during fat extraction process and the biomass does not require any further surface modification.

3.3. Characterization of biomass

FT-IR analysis gives us important information regarding the involvement of functional groups in the reaction/process studied. The FT-IR analysis of unloaded and Drimarine Yellow HF-3GL dye loaded *Trogoderma granarium* biomass (free and immobilized forms) is presented in Figs. 1 and 2, respectively. From Fig. 1(a), the presence of peak at 3,300 cm^{-1} indicates the involvement of O–H group on the surface of biomass. The peak at 1,650 cm^{-1} shows the presence of carbonyl group and peak at about 2,900 cm^{-1} is due to the C–H stretching. The disappearance of peak at 2,900 cm^{-1} was observed in case of immobilized biomass (Fig. 2(a)) which might be the reason of low adsorption capacity of immobilized form of biomass as compared with the free form of biomass. Due to specific interaction between biomass functional groups and dye molecules, a clear change in the % transmittance of peaks in dye loaded and unloaded spectra was observed. This interaction of functional groups and dye molecules resulted in vanishing and broadening of some peaks which confirms the involvement of these functional groups in adsorption process.

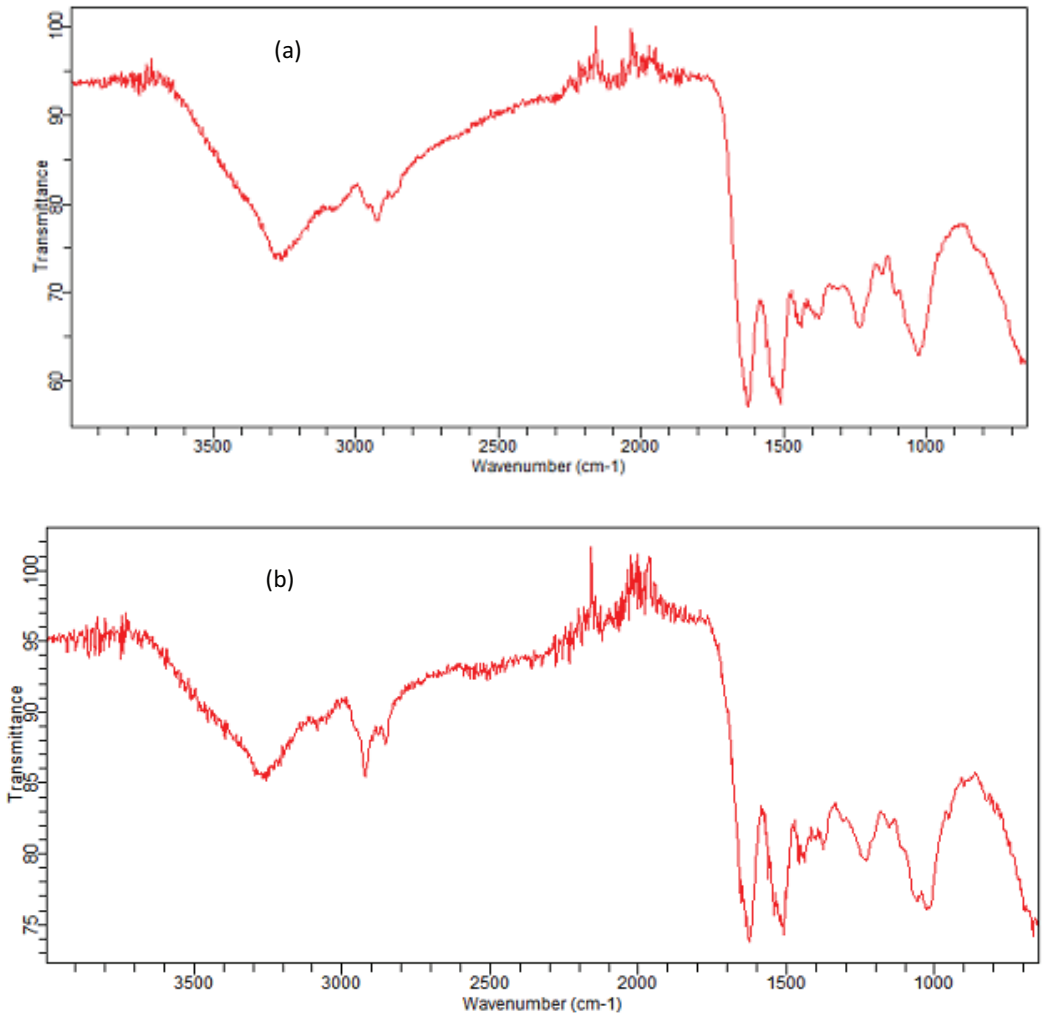

Fig. 1. FT-IR spectra of *Trogoderma granarium* de-oiled free form of (a) unloaded biomass and (b) Drimarine Yellow HF-3GL dye loaded biomass.

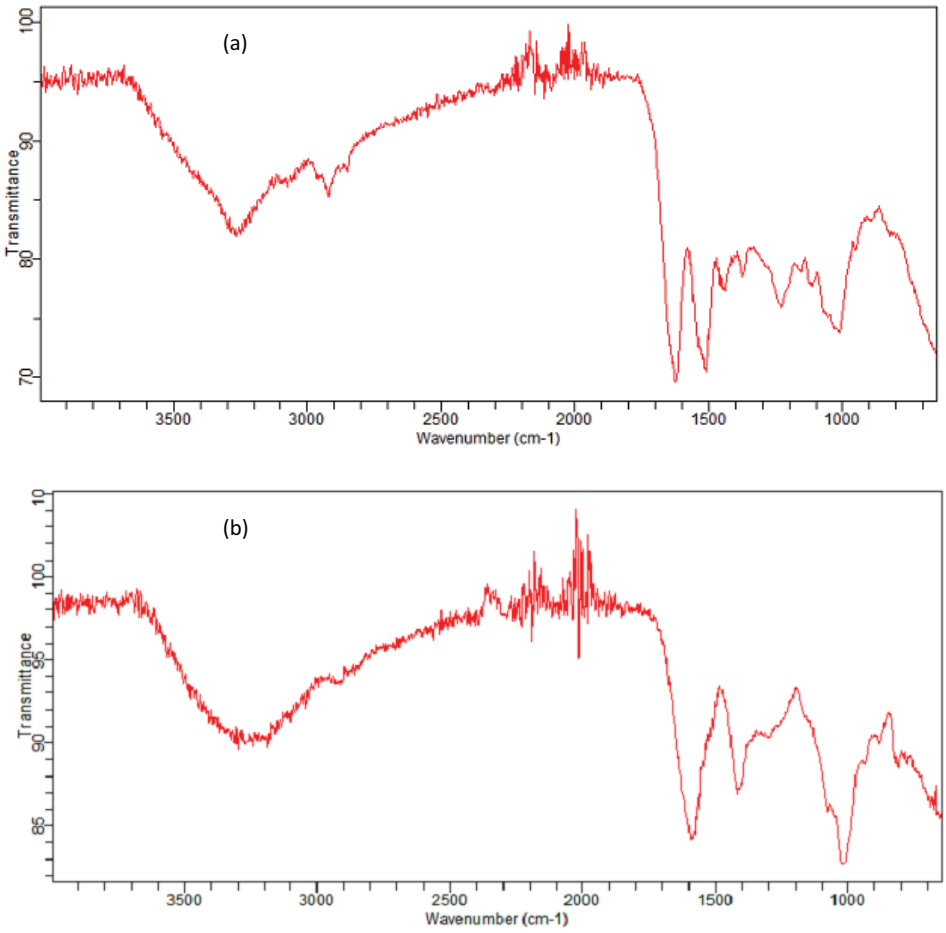

Fig. 2. FT-IR spectra of *Trogoderma granarium* de-oiled immobilized form of (a) unloaded biomass and (b) Drimarine Yellow HF-3GL dye loaded biomass.

pH_{pzc} is an important characteristic of biomass which should be determined in order to investigate the mechanism of adsorption process. It is the pH at which biomass carries no charge. Above this pH, it will carry negative charge and below this, it will carry positive charge. Point of zero charge of de-oiled *Trogoderma granarium* biomass was also determined by the method previously described in methodology section. The pH_{pzc} for free form of biomass was found to be 6.3 and for immobilized biomass, it was 7.0 (Fig. 3). This slight difference in the pH_{pzc} of free and immobilized biomass is due to the involvement of immobilization matrix. Adsorption of cations is favored at $pH > pH_{pzc}$ while adsorption of anions is favored at $pH < pH_{pzc}$. Below pH_{pzc}, the functional groups present on the surface of biomass become protonated which facilitate the adsorption of anionic dyes on the surface of biomass [31].

The surface features and morphological characteristics of the de-oiled insect biomass were studied by using SEM. It is used to determine the particle shape and porous structure of biomass. Greater number of pores shows greater adsorption capacity of biomass. Typical SEM photograph of *Trogoderma granarium* de-oiled biomass is shown in Fig. 4 which indicated the porous texture of the biomass with high heterogeneity that could contribute to the adsorption of the dye.

3.4. Batch adsorption study

3.4.1. Effect of pH

pH is a very influencing parameter in the adsorption process. The solution pH not only controls the availability of adsorbate molecules to the adsorbent but it also controls the activity of functional groups present on the surface of adsorbent [32]. To investigate the effect of this important parameter on the adsorptive removal of Drimarine Yellow HF-3GL dye by de-oiled biomass of *Trogoderma granarium* larvae, the solution pH was varied from 2 to 9. The experiment was performed with free and immobilized form of biomass to compare their adsorption potential (Fig. 5(a)). The results indicated that acidic range of pH was favorable for the removal of dye from aqueous solution. Maximum dye removal (20.2 mg/g) was achieved at pH 2 with free form of biomass. The adsorption potential of biomass was significantly reduced at higher pH values. This can be attributed due to the fact that at lower pH, the protonation of surface functional groups takes place which leads to the high attraction of biomass for the anionic dye molecules. At higher pH, the concentration of negatively charged species (OH^-) increases in the solution which creates a competition between anionic dye molecules and OH^- ions to adsorb on the surface of biomass. This factor overall results in

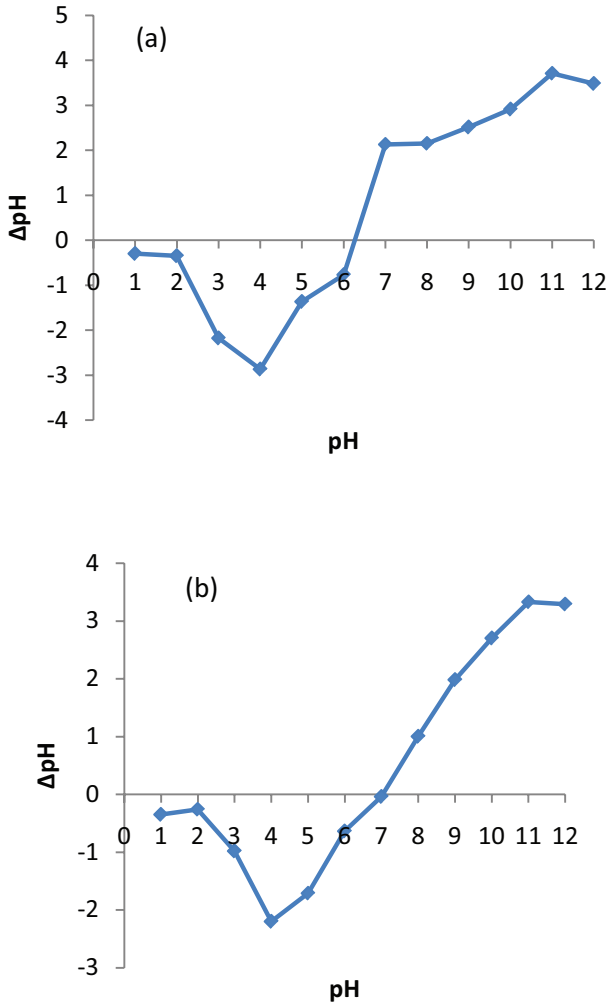

Fig. 3. Point of zero charge of (a) free and (b) immobilized de-oiled biomass of *Trogoderma granarium.*

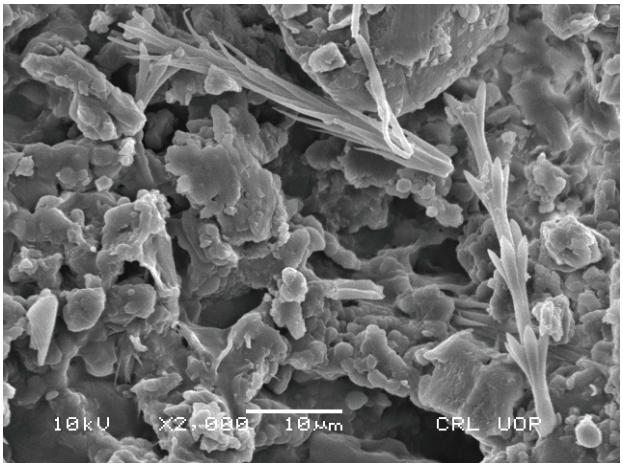

Fig. 4. SEM analysis of *Trogoderma granarium* de-oiled biomass.

decreased adsorption of dye molecules. The observed trend of favorable adsorption at acidic pH can also be confirmed by our results of pH_{pzc} determination. Many studies have been reported by different researchers in which anionic dye molecules show more adsorption onto the surface of biomass in acidic range of pH [33,34].

3.4.2. Effect of contact time and biosorbent dose

To investigate the optimum time required for attainment of equilibrium in adsorption process, the experiment was conducted by varying the reaction time from 0 to 240 min. The trial was conducted by using two different biomass doses (0.05 g/50 mL and 0.1 g/50 mL). The experimental results indicated that the adsorption process was fast initially. With the progress of time, the rate of adsorption becomes slower. Overall, the equilibrium was achieved within 15 min. After 15 min, no remarkable change in adsorption was observed. This might be due to the fact that in the start of reaction, large number of active sites is available for the adsorption of dye molecules. With the passage of time, the dye molecules get attached on the binding sites and active sites become saturated [35]. When no more active sites remain available for further adsorption, the equilibrium is achieved. In this study, the equilibrium was achieved in 15 min. The results are shown in Fig. 5(b) which clearly indicates that free form of biomass shows more adsorption potential as compared with the immobilized form of biomass. This might be due to the fact that immobilization may result in the blocking of active sites and dye molecules become unable to reach the active sites [36]. In case of immobilization of biomass, the biosorbent particles exist inside the immobilization matrix and dye molecules face resistance to reach the binding sites. These factors lead to the reduced adsorption capacity with immobilized biomass as compared with free form of biomass. The amount of biomass is also an influencing parameter as it helps in estimating the amount of biomass required for effective water treatment process. Among the two biomass dosages tested, the maximum dye removal was achieved with 0.05 g biomass. At higher biomass dosage (0.1 g), less removal of dye was observed. The decrease in the amount of dye adsorbed, q_e (mg/g) with increasing amount of biosorbent is due to the split in concentration gradient between solute concentration in the solution and solute concentration on the surface of the biomass [37]. Another factor is that when biomass concentration increases it may lead to the aggregation of particles which result in decreased effective surface area available for adsorption of dye and an increase in diffusion path length [38].

3.4.3. Effect of initial dye concentration

In the wastewater treatment process, the amount of pollutant in the aqueous solution also affects the overall treatment process. The higher amount of target pollutant provides a driving force to cope with the mass transfer resistance between solid and aqueous phase. The experiment was conducted by varying the initial dye concentration from 10 to 1,000 mg/L and results are shown in Fig. 5(c). The results indicated that with the increase in initial dye concentration of Drimarine Yellow HF-3GL dye, there was an increase in adsorption of dye onto the surface of de-oiled insect biomass. A sharp increase in adsorption capacity of biomass was observed when the initial dye concentration was varied from

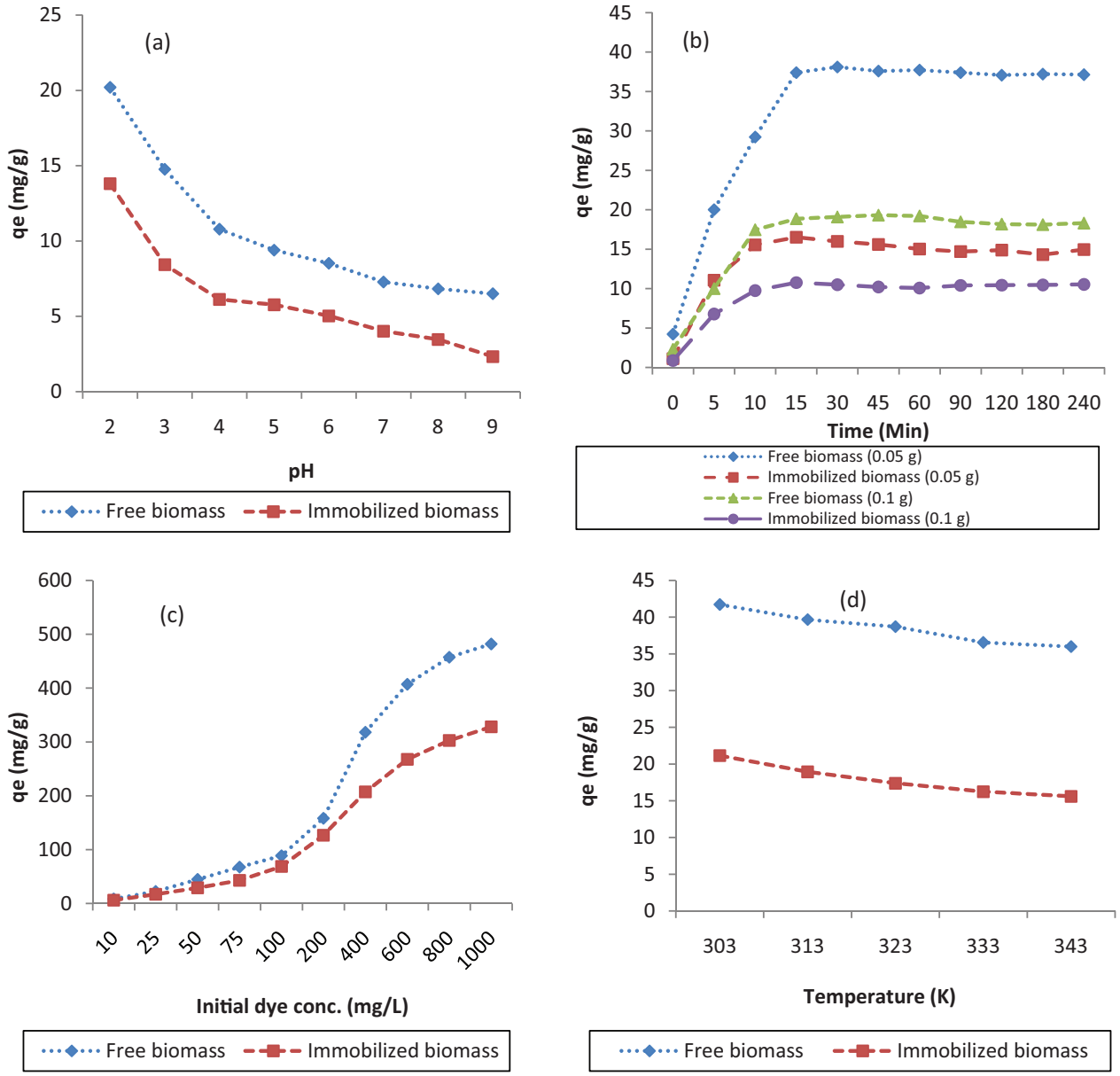

Fig. 5. Effect of (a) pH, (b) contact time and biomass dosage, (c) initial dye concentration and (d) temperature on the removal of Drimarine Yellow HF-3GL dye by using *Trogoderma granarium* de-oiled biomass.

10 to 600 mg/L. Above this concentration; the adsorption capacity further increased but not so remarkably as it was up to 600 mg/L. The maximum adsorption capacity was found to be 481.9 mg/g with free form of biomass and 328.1 mg/g with immobilized form of biomass. This shows that when the dynamic balance between dye concentration and biosorbent biomass surface takes place equilibrium is established [39]. The higher initial dye concentration results in boosting up the adsorption process.

3.4.4. Effect of temperature

Generally, the textile industries release the wastewater at higher temperatures hence the temperature of water can be an influencing parameter for the adsorption process. The experiment was conducted at different temperatures in order to see the effect of temperature on adsorption capacity of biomass. The range of temperature was selected from 303 to 343 K and results are shown in Fig. 5(d). The results show that maximum dye removal was obtained at 303 K. This shows exothermic nature of adsorption process. When temperature increased, the dye uptake capacity of adsorbent decreased. The decrease in adsorption capacity of *Trogoderma granarium* de-oiled biomass at higher temperature might be due to the weakening of attractive forces which are responsible for the attachment of dye molecules onto the surface of biomass [40]. Another reason can also be the deactivation of biomass active sites at higher temperatures which results in the decrease in adsorption capacity of biomass at higher temperatures [41].

3.5. Kinetic study

The study of rate controlling steps is an important factor during the designing of wastewater treatment systems. Different kinetic models have been applied on the experimental data to understand the kinetics of adsorption process. The applicability of kinetic models was determined by measuring the correlation coefficients (R^2).

Pseudo-first-order kinetic model is based on the fact that the change in dye concentration with respect to time is proportional to power one. The pseudo-first-order model is generally expressed as:

$$\log(q_e - q_t) = \log q_e - K_1 \cdot \frac{t}{2.303} \quad (3)$$

where q_e and q_t are the adsorption capacities (mg/g) at equilibrium and time t, respectively, K_1 is the rate constant (L/min) and t is the contact time (min). A graph is plotted between $\log(q_e - q_t)$ vs. t and the result of application of model on the experimental data is summarized in Table 1. By the application of this model, there is very poor correlation coefficient (R^2) and there was also very weak correlation between the experimental and predicted adsorption capacities. So results indicate incompatibility of pseudo-first-order kinetic model to the kinetic data.

Pseudo-second-order kinetic model is mostly applied to understand the mechanism of adsorption over a complete range of contact time.

The following expression is used for the application of pseudo-second-order kinetic model:

$$\left(\frac{t}{q_t}\right) = \frac{1}{K_2 q_e^{\,2}} + \frac{t}{q_e} \quad (4)$$

A plot between t/q_t vs. t gives the value of the constants K_2 (g/mg h) and q_e (mg/g). The pseudo-second order parameters K_2, q_e calculated, q_e experimental and R^2 for adsorption of Drimarine Yellow HF-3GL dye by *Trogoderma granarium* de-oiled biomass are presented in Table 1. Results indicated that the calculated and experimental q_e values are closer to each other and the value of correlation coefficient (R^2) is also very high. So, pseudo-second-order kinetic model show best fitness to the kinetic data and it is more appropriate and effective than pseudo-first-order kinetic model.

The adsorption process involves multiple steps starting from the movement of dye molecules in aqueous solution to the attachment of molecules onto the surface of biomass. Usually the batch systems involve fast and continuous stirring, so the rate controlling steps may involve the film diffusion, intra-particle diffusion or both. The intra-particle diffusion equation is written as follows:

$$q_t = K_{pi} t^{1/2} + C_i \quad (5)$$

where C_i is the intercept which describes the boundary layer thickness and K_{pi} (mg/g $\text{min}^{1/2}$) is the rate constant of intra-particle diffusion. The values of K_{pi} and C_i and R^2 for the adsorption of Drimarine Yellow HF-3GL dye by *Trogoderma granarium* de-oiled biomass are given in Table 1. The intra-particle diffusion model implies that the plot of q_t vs. $t^{1/2}$ should be linear. If the intra-particle diffusion is involved in the adsorption reaction, then a plot of the amount of the solid adsorbed per unit mass of adsorbent (q_t) against square root of time ($t^{1/2}$) should give a straight line and the particle diffusion would be the controlling step if this line passed through the origin [42]. The application of kinetic models on the experimental data has also been shown in Fig. 6. The poor value of correlation coefficient (R^2) indicates that the adsorption

Table 1
Kinetic modeling of data for the adsorptive removal of Drimarine Yellow HF-3GL dye by using *Trogoderma granarium* de-oiled biomass

Kinetic model	Free biomass (0.05 g)	Free biomass (0.1 g)	Immobilized biomass (0.05 g)	Immobilized biomass (0.1 g)
Pseudo-first order				
K_1 (L/min)	0.007	0.002	0	0.009
q_e experimental (mg/g)	38.12	19.32	16.51	10.75
q_e calculated (mg/g)	3.365	1.462	1.976	1.513
R^2	0.211	0.040	0.015	0.453
Pseudo-second order				
K_2 (g/mg min)	0.02	0.41	0.10	0.09
q_e experimental (mg/g)	38.12	19.32	16.51	10.75
q_e calculated (mg/g)	38.46	18.51	14.70	10.63
R^2	0.999	0.999	0.999	0.999
Intra-particle diffusion				
K_{pi}	1.49	0.67	0.44	0.38
C_i	21.46	11.60	10.44	6.459
R^2	0.448	0.356	0.239	0.382

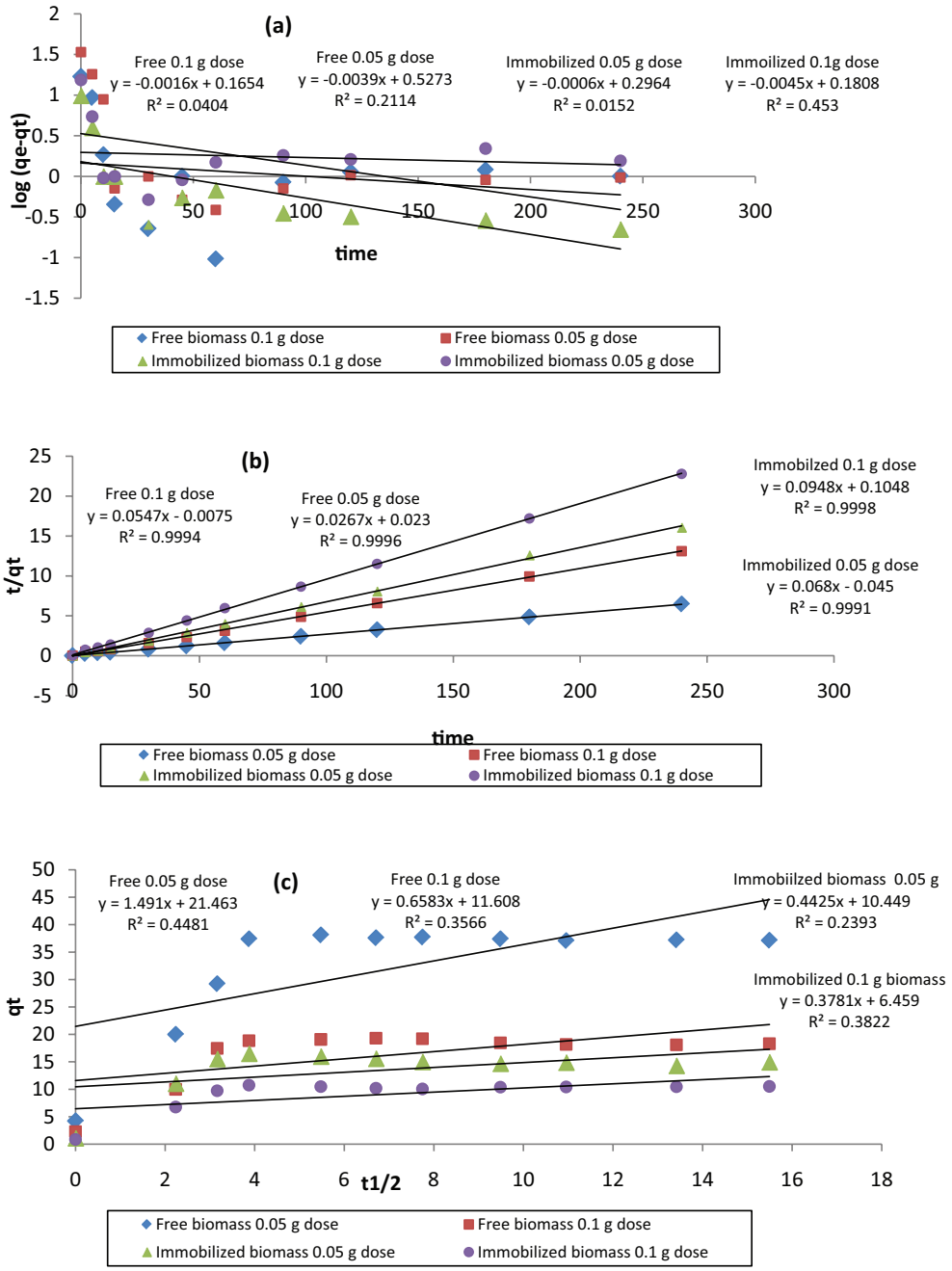

Fig. 6. Application of (a) pseudo-first order, (b) pseudo-second order and (c) intra-particle diffusion model on experimental data for removal of Drimarine Yellow HF-3GL dye by *Trogoderma granarium* de-oiled biomass.

of Drimarine Yellow HF-3GL dye by *Trogoderma granarium* de-oiled biomass did not follow intra-particle diffusion model.

3.6. Equilibrium study

Different equilibrium models have been applied by different researchers to understand the mechanism of adsorption process. If the adsorption process obeys chemisorption then Langmuir adsorption isotherm will show good correlation with the experimental results. The linear form of Langmuir model can be written as:

$$\frac{C_e}{q_e}=\frac{1}{q_m b}+\frac{C_e}{q_m} \tag{6}$$

Here q_m is the maximum adsorption capacity (mg/g) and b is the value for Langmuir constant. This constant b gives us the information about the energy of adsorption (L/mg). These values can be obtained by plotting a graph between C_e/q_e vs. C_e.

R_L is also an important characteristic of Langmuir adsorption isotherm model. It is dimensionless and constant separation factor for equilibrium parameter. The significance

of this dimensionless constant is that its value can help in indicating whether the isotherm is favorable, unfavorable or linear as for favorable isotherm R_L ($0 < R_L < 1$), unfavorable ($R_L > 1$), irreversible ($R_L = 0$) or linear ($R_L = 1$). It can be calculated as [43]:

$$R_L = \frac{1}{1 + bC_o} \tag{7}$$

C_o is the initial dye concentration and b is the Langmuir constant. The values of Langmuir constants and R^2 for the adsorption of Drimarine Yellow HF-3GL dye by *Trogoderma granarium* de-oiled biomass are presented in Table 2 which shows best fitness of model for adsorption of dye onto both forms of biomass. Also there is a close relation between the experimental and calculated values of adsorption capacities which also confirm the fitness of Langmuir model on the experimental results. This shows that the mechanism of Drimarine Yellow HF-3GL dye adsorption onto *Trogoderma granarium* de-oiled biomass is chemisorption and monolayer.

If the adsorption process obeys multilayered adsorption process which is due to physical adsorption then Freundlich adsorption isotherm model will show good correlation with the experimental results. Freundlich adsorption isotherm model assumes that the surface of biomass has heterogeneous nature. It deals with the interaction between adsorbed molecules and a non-uniform distribution of heat of sorption over the surface. Mathematically it can be expressed as:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{8}$$

where q_e is the amount of dye adsorbed per unit of adsorbent at equilibrium time (mg/g), C_e is the equilibrium concentration of dye in solution (mg/L). The constant K_F indicates the adsorption capacity. Another constant n helps to measure the deviation from linearity of the adsorption and is used to verify types of adsorption. It is suggested that if n is equal to unity, the adsorption is linear, n below unity indicates that adsorption is a chemical process; whereas, n above unity is associated with a favorable adsorption [44]. The experimental results for the application of Freundlich adsorption isotherm model are presented in Table 2 which shows poor fitness of Freundlich model on the experimental results.

The Temkin isotherm model suggests an equal distribution of binding energies over the number of the exchanging sites on the surface of biomass.

The linear form of Temkin isotherm can be written as:

$$q_e = B\ln A + B\ln C_e \tag{9}$$

where $B = RT/b$, T is the absolute temperature in Kelvin, b is the Temkin constant and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). A is the equilibrium binding constant and B is corresponding to the heat of sorption. These constants and R^2 values can be calculated by plotting graph between q_e and lnC_e. The value of R^2 and other constants are presented in Table 2.

The multilayered adsorption phenomena can be explained by Harkins–Jura isotherm model on the basis of heterogeneous pore distribution. The linear form of the Harkins–Jura isotherm model is presented in equation below:

$$\frac{1}{q_e^{\,2}} = \left(\frac{B}{A}\right) - \left(\frac{1}{A}\right)\log C_e \tag{10}$$

The values of Harkins–Jura constants are shown in Table 2.

The D–R isotherm model is used for estimation of the porosity apparent free energy. The linear form of D–R isotherm model can be seen below:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{11}$$

where β is a constant corresponding to the adsorption energy, q_m is the theoretical saturation capacity and ε is the Polanyi potential which is calculated from equation below:

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \tag{12}$$

Table 2
Equilibrium modeling of data for the adsorptive removal of Drimarine Yellow HF-3GL dye by using *Trogoderma granarium* de-oiled biomass

Equilibrium model	Free biomass	Immobilized biomass
Langmuir		
q_m experimental (mg/g)	481.9	328.1
q_m calculated (mg/g)	555.5	454.5
b	0.013	0.004
R_L	0.6	0.83
R^2	0.99	0.97
Freundlich		
K_F	11.96	3.4
n	1.51	1.33
R^2	0.93	0.95
Temkin		
A	3.68	8.13
B	94.6	68.4
R^2	0.94	0.93
Harkins–Jura		
A	303	16.3
B	2.03	2.26
R^2	0.4	0.36
Dubinin–Radushkevich		
q_m (mg/g)	180.4	159.6
$\beta \times 10^4$ (mol^2/kJ^2)	0.002	0.009
E (kJ/mol)	15.8	7.45
R^2	0.62	0.58

where R (8.314 J mol^{-1} K^{-1}) is the gas constant and T (K) is the absolute temperature. The mean free energy of adsorption E can be defined as the free energy change when 1 mole of ion is transferred from infinity in solution to the adsorbent. E can be calculated from the β value by the following relation:

$$E = 1/(2\beta)^{1/2} \quad (13)$$

E gives us information about adsorption mechanism. When 1 mole of ions is transferred, the value range 1–8 kJ/mol indicates physical adsorption [45], the value of E between 8 and 16 kJ/mol indicates the adsorption process, followed by ion-exchange mechanism [46] while its value in the range of 20–40 kJ/mol is indicative of chemical adsorption [47]. The values of D–R parameters are presented in Table 2 and adsorption curves can be seen in Fig. 7.

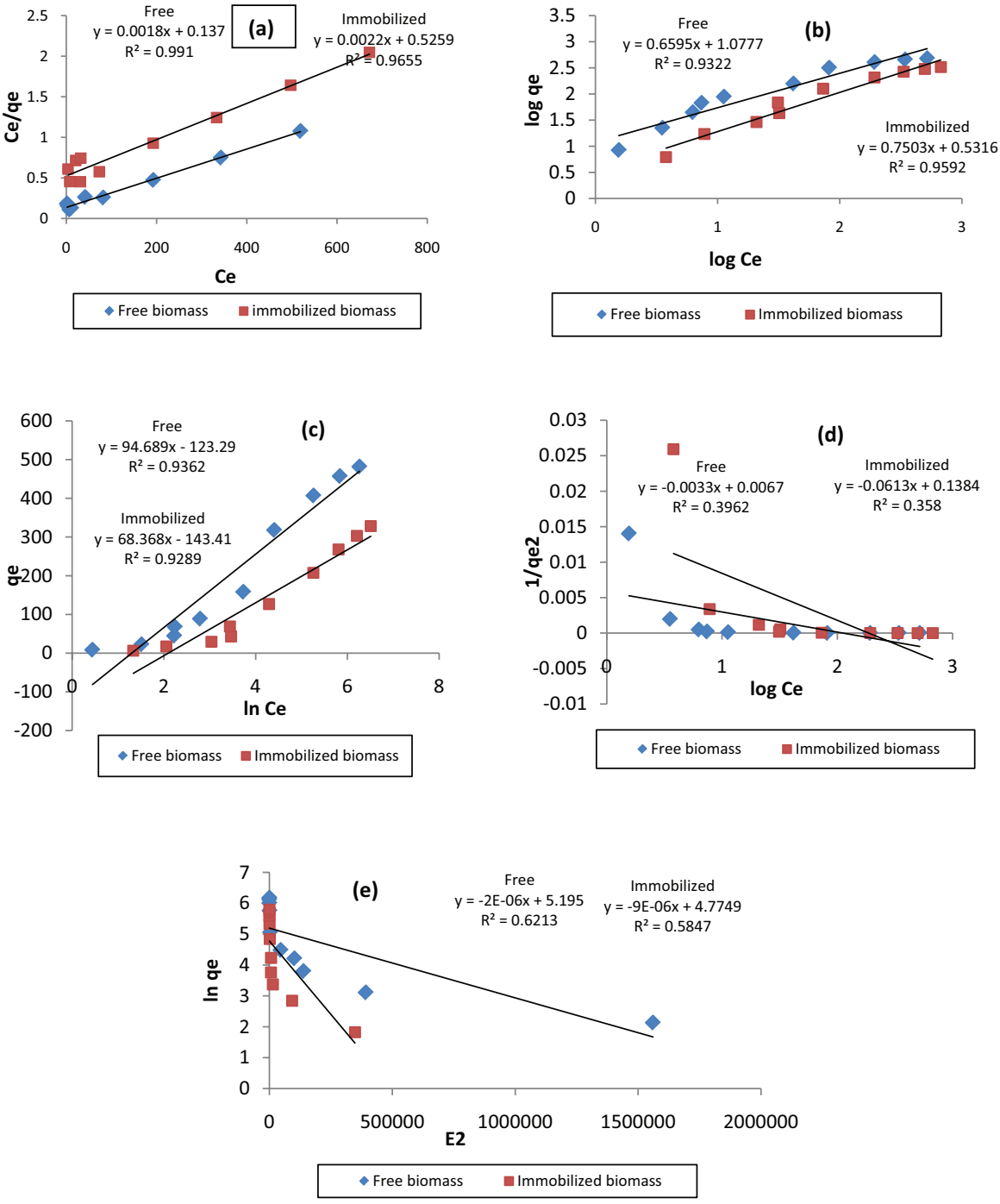

Fig. 7. Application of (a) Langmuir, (b) Freundlich, (c) Temkin, (d) Harkins–Jura and (e) D–R model on experimental data for removal of Drimarine Yellow HF-3GL dye by *Trogoderma granarium* de-oiled biomass.

3.7. Thermodynamic study

The experimental data obtained from the optimization of temperature were used for the thermodynamic study. As we know that:

$$\Delta G^\circ = -RT\ln K_d \tag{14}$$

where $K_d = q_e/C_e$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{15}$$

R is the gas constant (8.314 J/mol K) and T is the absolute temperature.
so it can also be written as:

$$\ln(K_d) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \times \frac{1}{T} \tag{16}$$

The graph is plotted between $\ln K_d$ and $1/T$. The values of ΔH and ΔS are obtained from slope and intercept of graph. The result of thermodynamic study for the adsorption of Drimarine Yellow HF-3GL dye by *Trogoderma granarium* de-oiled biomass is summarized in Table 3. Negative value of ΔS indicates the decrease in entropy during adsorption process which is due to the shifting of randomly moving dye molecules from solution onto the adsorbate surface [48]. Hence adsorption reduces the overall entropy of system. The negative value of ΔG indicates that adsorption process is spontaneous and feasible. The exothermic nature of process is also confirmed by the negative value of enthalpy change. The overall results are compiled in Table 3.

3.8. Desorption study

Desorption study was conducted to check out the possibility of reuse of adsorbent and adsorbate. The regeneration of biomass and adsorbate is environment friendly and it makes the adsorption process economical when applied on large scale. Desorption was checked by using HCl and NaOH. Desorption study was conducted with different acid and alkali concentrations ranging from 0.2% to 1%. Among the alkali and acidic solutions, the 0.4% NaOH solution was found to be favorable for desorption of 78.7% adsorbed dye. This might be due to the fact that anionic dye shows good attachment at acidic range of pH so in order to desorb the attached molecules, alkaline range of solution pH will be favorable.

4. Conclusion

The study was focused on the utilization of *Trogoderma granarium* de-oiled biomass for the removal of a synthetic dye (Drimarine Yellow HF-3GL) from aqueous solutions. Pretreatment of biomass was done in order to enhance the adsorption capacity of biomass but the residual biomass has not shown any remarkable change in its adsorption capacity after treatment with acids and base. The adsorption capacity of biomass was found to be 481.9 mg/g for Drimarine Yellow HF-3GL dye by keeping solution pH 2 and temperature 30°C. Immobilized biomass has low adsorption potential as compared with free form of biomass. Langmuir adsorption isotherm was found to be best fit on the experimental data. The adsorption kinetics obeys pseudo-second-order kinetic model. Thermodynamic study showed that the process was exothermic in nature. The residual insect biomass has shown higher adsorption capacity as compared with various lignocellulosic materials which have been reported earlier in literature for the treatment of textile effluents [11,49,50]. Overall, the study results indicated that the *Trogoderma granarium* de-oiled biomass can be used as a potential adsorbent for the wastewater treatment.

Closing remarks

In the field of bio-energy, the major focus of every researcher is to explore the sustainable and cheap alternative resources which can be converted into environment friendly and good quality biofuels. A lot of work has been done in this field but the major constraint in the commercialization of biofuels is their production cost. This high cost of biofuel production can be offset by using the residual biomass of bio-energy processes for some potential applications such as treatment of wastewaters.

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Table 3
Thermodynamic study for the adsorptive removal of Drimarine Yellow HF-3GL dye by using *Trogoderma granarium* de-oiled biomass

Temperature(K)	Free biomass			Immobilized biomass		
	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol/K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol/K)
303	–4.07	–15.23	–37.08	0.78	–10.3	–36.8
313	–3.50			1.31		
323	–3.31			1.65		
333	–2.77			2.02		
343	–2.59			2.25		

References

[1] S.P. Singh, P. Singh, Effect of CO_2 concentration on algal growth: a review, Renew. Sust. Energy Rev., 38 (2014) 172–179.
[2] P.J.L. William, L.M.L. Laurens, Microalgae as biodiesel and biomass feedstock: review and analysis of the biochemistry, energetic and economics, Energy Environ. Sci., 3 (2010) 554–590.
[3] Q. Hu, M. Sommerfeld, E. Jarvis, M. Ghirardi, M. Posewitz, M. Seibert, A. Darzins, Microalgal triacylglycerols as feedstocks for biofuel production: perspectives and advances, Plant J., 54 (2008) 621–639.
[4] N.V. Kulkarni, S. Gupta, R. Kataria, N. Sathyanarayana, Morphometric analysis and reproductive system studies of *Trogoderma granarium* Everts (Coleoptera: Dermestidae), Int. J. Sci. Res. Publ., 5 (2015) 1–8.
[5] J.A. Kerr, Khapra beetle returns, Pest control, 49 (1981) 24–25.
[6] M.A. Arain, T. Ahmad, M. Afzal, Preliminary studies on khapra beetle *Trogoderma granarium* Everts infestation in wheat under lab conditions, Pak. Entomol., 28 (2006) 27–29.
[7] M.S. Ahmedani, A. Khaliq, M. Tariq, M. Anwar, S. Naz, Khapra beetle (*Trogoderma granarium* Everts): a serious threat to food security and safety, Pak. J. Agric. Sci., 44 (2007) 481–493.
[8] S. Lowe, M. Browne, S. Boudjelas, M. DePoorter, 100 of the World's Worst Invasive Alien Species: A Selection from the Global Invasive Species Database, Invasive Species Specialist Group, World Conservation Union (IUCN), 2000. Available at: http:// www.issg.org/database/species/reference_files/100English.
[9] Z. Li, D. Yang, M. Huang, X. Hu, J. Shen, Z. Zhao, J. Chen, *Chrysomya megacephala* (Fabricius) larvae: a new biodiesel resource, Appl. Energy, 94 (2012) 349–354.
[10] S. Chowdhury, P. Das, Utilization of a domestic waste eggshells for removal of hazardous malachite green from aqueous solutions, Environ. Prog. Sust. Energy., 3 (2012) 415–425.
[11] S. Sadaf, H.N. Bhatti, S. Nausheen, M. Amin, Application of a novel lignocellulosic biomaterial for the removal of Direct Yellow 50 dye from aqueous solution: batch and column study, J. Taiwan Inst. Chem. Eng., 47 (2015) 160–170.
[12] T. Akar, B. Anilan, A. Gorgulu, S.T. Akar, Assessment of cationic dye biosorption characteristics of untreated and non-conventional biomass: *Pyracantha coccinea* berries, J. Hazard. Mater., 168 (2009) 1302–1309.
[13] S. Peretz, O. Cinteza, Removal of some nitrophenol contaminants using alginate gel beads, Colloids Surf., A, 319 (2008) 165–172.
[14] S. Sadaf, H.N. Bhatti, Batch and fixed bed column studies for the removal of Indosol Yellow BG dye by peanut husk, J. Taiwan Inst. Chem. Eng., 45 (2014) 541–553.
[15] Y.P. Ting, G. Sun, Use of polyvinylalcohol as a cell immobilization matrix for copper biosorption by yeast cells, J. Chem. Technol. Biotechnol., 75 (2000) 541–546.
[16] G. Bayramoglu, A. Denizli, S. Bektas, M.Y. Arica, Entrapment of *Lentinus sajor-caju* into Ca-alginate gel beads for removal of Cd(II) ions from aqueous solution: preparation and biosorption kinetics analysis, Microchem. J., 72 (2002) 63–76.
[17] H.N. Bhatti, R. Khalid, M.A. Hanif, Dynamic biosorption of Zn (II) and Cu (II) using pretreated Rosa gruss an teplitz (red rose) distillation sludge, Chem. Eng. J., 148 (2009) 434–443.
[18] S. Lagergren, Zur theorie der sogenannten adsorption gelster stoffe, K. Sven. Vetensk.akad. Handl., 24 (1898) 1–39.
[19] Y.S. Ho, G. Mckay, D.A.J. Wase, C.F. Foster, Study on the sorption of divalent metal ions onto peat, Adsorpt. Sci. Technol., 18 (2000) 639–650.
[20] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanitary. Eng. Div., Am. Soc. Civ. Eng., 89 (1963) 31–59.
[21] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc., 40 (1918) 1361–1403.
[22] H.M.F. Freundlich, Ober die adsorption in Losungen, J. Phys. Chem., 57 (1906) 385–470.
[23] M.J. Temkin, V. Pyzhev, Recent modifications to Langmuir isotherms, Acta Physiochim URSS, 12 (1940) 217–222.
[24] W.D. Harkins, C.J. Jura, Surfaces of Solids XIII. A vapor adsorption method for the determination of the area of a solid without the assumption of a molecular area, and the areas occupied by nitrogen and other molecules on the surface of a solid, J. Am. Chem. Soc., 66 (1944) 1366–1373.
[25] M.M. Doubinin, L.V. Radushkevich, Proceedings of the academy of sciences of the USSR, Phys. Chem., 55 (1947) 327–329.
[26] I.D. Mall, V.C. Shrivastava, G.V.A. Kumar, I.M. Mishra, Characterization and utilization of mesoporous fertilizer plant waste carbon for adsorptive removal of dyes from aqueous solution, Colloids Surf., A, 278 (2006) 175–187.
[27] Q. Li, L. Zheng, Y. Hou, S. Yang, Z. Yu, Insect fat, a promising resource for biodiesel, J. Pet. Environ. Biotechnol., S2 (2011) 001.
[28] Z.H. Levinson, P.H. Silverman, Studies on the Lipids of *Musca vicina* (Macq.) during growth and metamorphosis, Biochem. J., 58 (1954) 294–297.
[29] R. Ahmad, R. Kumar, Adsorption studies of hazardous malachite green onto treated ginger waste, J. Environ. Manage., 91 (2010) 1032–1038.
[30] S. Dawood, T.K. Sen, Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: equilibrium, thermodynamic, kinetics, mechanism and process design, Water Res., 46 (2012) 1933–1946.
[31] D. Savova, N. Petrov, M.F. Yardim, E. Ekinci, T. Budinova, M. Razvigorova, V. Minkova, The influence of the texture and surface properties of carbon adsorbents obtained from biomass products on the adsorption of manganese ions from aqueous solution, Carbon, 41 (2003) 1897–1903.
[32] W.S. Alencar, E. Acayanka, E.C. Lima, B. Royer, F.E. de Souza, J. Lameira, Application of *Mangifera indica* (mango) seeds as a biosorbent for removal of Victazol Orange 3R dye from aqueous solution and study of the biosorption mechanism, Chem. Eng. J., 209 (2012) 577–588.
[33] A. Esmaeli, M. Jokar, M. Kousha, E. Daneshvar, H. Zilouei, K. Karimi, Acidic dye wastewater treatment onto a marine macroalga, *Nizamuddina zanardini* (Phylum: Ochrophyta), Chem. Eng. J., 217 (2013) 329–336.
[34] M. Asgher, H.N. Bhatti, Mechanistic and kinetic evaluation of biosorption of reactive azo dyes by free, immobilized and chemically treated *Citrus sinensis* waste biomass, Ecol. Eng., 36 (2010) 1660–1665.
[35] Y. Hamzeh, A. Ashori, E. Azadeh, A. Abdulkhani, Removal of Acid Orange 7 and Remazol Black 5 reactive dyes from aqueous solutions using a novel biosorbent, Mater. Sci. Eng. C, 32 (2012) 1394–1400.
[36] K. Vijayaraghavan, J. Maoa, Y.S. Yun, Biosorption of methylene blue from aqueous solution using free and polysulfone immobilized *Corynebacterium glutamicum*: batch and column studies, Bioresour. Technol., 99 (2008) 2864–2871.
[37] P.S. Kumar, S. Ramalingam, C. Senthamarai, M. Niranjanaa, P. Vijayalakshmi, S. Sivanesan, Adsorption of dye from aqueous solution by cashew nut shell: studies on equilibrium isotherm, kinetics and thermodynamics of interactions, Desalination, 261 (2010) 52–60.
[38] H.B. Senturk, D. Ozdes, C. Duran, Biosorption of Rhodamine 6G from aqueous solutions onto almond shell (*Prunus dulcis*) as a low cost biosorbent, Desalination, 252 (2010) 81–87.
[39] Z. Bouberka, A. Khenifi, N. Benderdouche, Z. Derriche, Removal of Supranol Yellow 4GL by adsorption onto Cr-intercalated montmorillonite, J. Hazard. Mater., 133 (2006) 154–161.
[40] M. Asgher, H.N. Bhatti, Evaluation of thermodynamics and effect of chemical treatments on sorption potential of Citrus waste biomass for removal of anionic dyes from aqueous solutions, Ecol. Eng., 38 (2012) 79–85.
[41] Z. Aksu, I.A. Isoglu, Use of agricultural waste sugar beet pulp for the removal of Gemazol turquoise blue-G reactive dye from aqueous solution, J. Hazard. Mater., 137 (2006) 418–430.
[42] K.G. Bhattacharyya, S.S. Gupta, Adsorption of Fe (III) from water by natural and acid activated clays: studies on equilibrium isotherm, kinetics and thermodynamics of interactions, Adsorption, 12 (2006) 185–204.
[43] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions, Int. Eng. Chem. Fundam., 5 (1966) 212–223.

[44] M.A.M. Salleh, D.K. Mahmoud, W.A. Karim, A. Idris, Cationic and anionic dye adsorption by agricultural solid wastes: a comprehensive review, Desalination, 280 (2011) 1–13.
[45] M.S. Onyango, Y. Kojima, O. Aoyi, E.C. Bernardo, H. Matsuda, Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9, J, Colloid Interface Sci., 279 (2004) 341–350.
[46] F. Helfferich, Ion Exchange, McGraw-Hill Book, Co., New York, NY, 1962.
[47] S.S. Tahir, N. Rauf, Removal of cationic dye from aqueous solutions by adsorption onto bentonite clay, Chemosphere, 63 (2006) 1842–1848.
[48] A. Mittal, J. Mittal, A. Malviya, V.K. Gupta, Removal and recovery of Chrysoidine Y from aqueous solutions by waste materials, J. Colloid Interface Sci., 344 (2010) 497–507.
[49] S. Sadaf, H.N. Bhatti, Evaluation of peanut husk as a novel, low cost biosorbent for the removal of Indosol Orange RSN dye from aqueous solutions: batch and fixed bed studies, Clean Technol. Environ. Policy, 16 (2014) 527–544.
[50] S. Sadaf, H.N. Bhatti, M. Arif, M. Amin, F. Nazar, Box-Behnken design optimization for the removal of Direct Violet 51 dye from aqueous solution using lignocellulosic waste, Desal. Wat. Treat., 56 (2015) 2425–2437.