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Calcined eggshell as a cost effective material for removal of dyes from aqueous solution

A. V. Borhade[1] · A. S. Kale[1]

Abstract The removal of Rhodamine B, Eriochrome black T and Murexide dyes from aqueous solutions using calcined eggshell powder were investigated. In this study, calcined eggshell powder was applied for its potential use as an adsorbent for the removal of Rhodamine B, Eriochrome black T and Murexide dyes from their aqueous solutions. The calcined eggshell powder obtained was characterized by Fourier Transform Infrared Spectroscopy (FT-IR), Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD). The various parameters such as initial concentration, pH, adsorbent dose and contact time were studied. Various isotherms including Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models were applied for the equilibrium adsorption data. The kinetic study of Rhodamine B, Eriochrome black T and Murexide dyes on calcined eggshell powder follows pseudo-second order kinetics.

Introduction

Water of high and acceptable quality is essential for living beings. In the life cycle of living beings water is essentially used for drinking, in cleaning, in industry and in agriculture. Today water pollution has become a serious issue

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before the society and researchers working in the respective field. Major sources of wastewater are industries like textile, paper, rubber, plastic, leather, cosmetic, food and drug industries (Robinson et al. 2001). Many organic dyes are also responsible for the water pollution discharged from paper, textile and dyes industries. This wastewater is very hazardous for the human health. About 100,000 dyes are commercially available and more than 8×10^5 tons of these dyes are produced annually worldwide (Robinson et al. 2001). It is reported that about 70–80% of illnesses causes due to water pollution (Bhatnagar and Minocha 2008). These dyes can cause allergic dermatitis, skin irritation, cancer and mutation in living organisms (Forgacs et al. 2004).Various methods are available to remove these dyes like coagulation (Stephenson and Sheldon 1996), precipitation (Stephenson and Sheldon 1996), reverse osmosis (Forgacs et al. 2004), photo-degradation (Wu et al. 1999), electrochemical oxidation (Kusvuran et al. 2004), ozonation (Robinson et al. 2001), and adsorption.

Adsorption is an effective method for removal of dyes from aqueous solution. Activated carbon is the widely used adsorbent for the removal of dyes (Wu et al. 1999). But it is costly, and therefore, it is very important to develop an alternative low-cost adsorbent. A variety of low-cost adsorbents are clay materials, zeolites, siliceous materials, coffee husk-based activated carbon, decreased coffee bean, marine algae, chitosan and ion exchange resin have been used for the removal of dyes from aqueous solution (Kyzas 2012; Ahmad and Rahman 2011; Baek et al. 2010). In the present study, eggshell powder is used as an adsorbent for the removal of dyes from aqueous solution. It contains more percentage of calcium carbonate and less amount of magnesium carbonate, calcium phosphate.

The literature survey reveals that the adsorbents available are costly and requires elaborate and complicated

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methods for their synthesis. In the present study, we have developed low-cost adsorbent using waste eggshell. This method is eco-friendly and highly efficient for the removal of dyes from their aqueous medium. This low-cost adsorbent finds highly efficient adsorbent for the removal of Rhodamine B, Eriochrome black T and Murexide dyes. The different parameters includes initial concentration, pH, adsorbent dosage and contact time were also studied. The adsorption isotherms and kinetic parameters are also summarised. This study enabled us to verify Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms. Further this paper also depicts verification of kinetic models including first order and second order kinetic models.

Experimental section

Adsorbate

Three dyes namely Rhodamine B, Eriochrome black T and Murexide are used in the present study for adsorption experiments. The chemical names and their properties are listed in Table 1. The dyes stock solution was prepared by dissolving accurate weight of it in deionised water to the concentration of 100 mg/L.
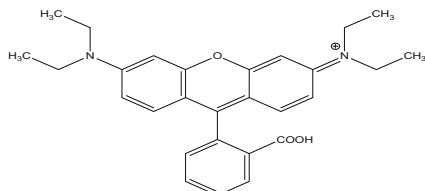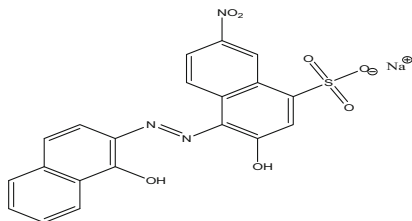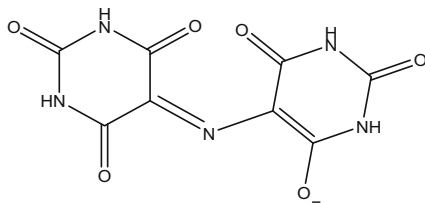
Adsorbent

The eggshell used in the study was collected from local market, Nasik, Maharashtra. First, the eggshells were washed with tap water and then with distilled water to remove dirt particles and dried for 2 h in the oven at 120 °C. Then it is allowed to cool at room temperature, subsequently crushed and then finally sieved to prepare fine powder. The dried calcined eggshell powder of about 90–100 micron size is used for the study. The elemental analysis shows eggshell powder contains 94% calcium carbonate, 4% magnesium carbonate, 3% protein and 1% organic matter (Bashir and Manusamy 2015).

Batch adsorption studies

The effect of different parameters such as adsorbate concentration, adsorbent dose and contact time were studied. A definite weight of calcined eggshell powder was added into 50 mL of dyes solution with initial concentration of 1–10 mg/L which is prepared from 1000 mg/L of dyes stock solutions. The contents were shaken thoroughly. The solutions were then filtered at present time interval and residual metal concentration was measured using Spectrophotometric method.

Table 1 The chemical structure, chemical formula and λ_{max} of the dyes

Dyes	Chemical structure	Molecular formula	Molecular weight, g mol^{-1}	λ_{max}
Rhodamine B		$C_{28}H_{31}Cl\,N_2O_3$	469.5	554
Eriochrome black T		$C_{20}H_{12}N_3O_7SNa$	461.381	503
Murexide		$C_8H_8N_6O_6$	284.19	525

Characterizations

Calcined eggshell powder was characterized by appropriate physiochemical techniques including FT-IR, XRD, SEM-EDAX, and TGA. IR adsorption study (KBr Pellets) was performed on a Shimadzu, 8400-S FT-IR spectrometer in the range of 4000–400 cm^{-1}. The phase purity of the product was performed by X-ray powder diffraction pattern using Rigaku Ultima IV copper instrument operating at 25 kV and 25 mA using Kα radiation with wavelength $\lambda = 0.154$ nm. Surface morphology and elemental analysis were studied by scanning electron microscopy JEOL-JEM-6360A model equipment JEOL-JEC-560 autocation coater, and Thermogravimetric analysis was performed on DTG-60 (SHIMADZU).

Theory

Adsorption

Adsorption is the phenomenon in which matter is extracted from one phase and concentrated at the surface of a second phase. The adsorption performance does not always depend only on the experimental condition and waste. Sometimes adsorption performance will depend on analytical method used for decontamination test like batch method, column, reactors, etc. (Bansal and Goyal 2005). In biosorption, we can remove heavy metal from dilute aqueous solution with the help of living system. In biosorption, we can also use dead biomass (Mohan and Pitman 2006).

Isotherms

Langmuir adsorption isotherm

This describes quantitatively the formation of a uniform and homogeneous monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases (Vermeulen et al. 1966). The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The linear form of Langmuir adsorption equation is

$$\frac{1}{Q_e} = \frac{1}{Q_o} + \frac{1}{Q_o K_L C_e} \tag{1}$$

where C_e is the equilibrium concentration of adsorbate (mg/L^{-1}), Q_e is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g), Q_o is the maximum monolayer coverage capacity (mg/g), K_L is the Langmuir isotherm constant (L/mg).

The values of K_L and q_m were computed from the slope and intercept of the Langmuir plot of $1/Q_e$ versus $1/C_e$ (Langmuir 1918). The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter (Webber and Chakravarti 1974).

$$R_L = \frac{1}{1 + (1 + K_L C_0)} \tag{2}$$

R_L value indicates the adsorption nature to be either unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$.

Freundlich adsorption isotherm

This is mainly used to describe the adsorption characteristics for the heterogeneous surface (Hutson and Yang 1997). The results obtained fit well to the linear format Freundlich isotherm,

$$\log Q_e = \log K_f + 1/n \log C_e \tag{3}$$

where K_f is the Freundlich isotherm constant (mg/g), n is the adsorption intensity.

The constant K_f is an approximate indicator of adsorption capacity, while $1/n$ is a function of the strength of adsorption in the adsorption process (Voudrias et al. 2002). If $n = 1$ then the partition between the two phases are independent of the concentration. If value of $1/n$ is below one it indicates a normal adsorption. On the other hand, $1/n$ being above one indicates cooperative adsorption (Mohan and Karthikeyan 1997). The function has an asymptotic maximum as pressure increases without bound. With the increase in temperature, the constants k and n change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface. However, K_f and n are parameters characteristic of the sorbent–sorbate system, which must be determined by data fitting, whereas linear regression is generally used to determine the parameters of kinetic and isotherm models (Guadalupe et al. 2008). Specifically, the linear least-squares method and the linearly transformed equations have been widely applied to correlate sorption data where $1/n$ is a heterogeneity parameter, the smaller $1/n$, the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm when $1/n = 1$. If n lies between one and ten, this indicates a favourable sorption process (Goldberg 2005).

Temkin adsorption isotherm

Adsorption–desorption interactions are given in a very specific manner by this isotherm. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage (Tempkin and Pyzhev 1940; Aharoni and Ungarish 1977). As indicated in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity sorbed Q_e against $\ln C_e$ and the constants were determined from the slope and intercept. The model is given in the linear form as (Tempkin and Pyzhev 1940)

$$Q_e = B \ln A_T + B \ln C_e \tag{4}$$

$$B = \frac{RT}{b_T}$$

A_T is the Temkin isotherm equilibrium binding constant (L/g), b_T is the Temkin isotherm constant, R is the universal gas constant (8.314 J/mol/K), T is the temperature at 298 K, B is the constant related to heat of sorption (J/mol).

Dubinin–Radushkevich isotherm

Gaussian energy distribution onto a heterogeneous surface (Gunay et al. 2007; Aharoni et al. 2001) is studied by Dubinin–Radushkevich isotherm. The model has often successfully fitted high solute activities and the intermediate range of concentrations data well. The linear form of this model is given by the equation

$$\ln Q_e = \ln (Q_s) - \left(K_{ad}\varepsilon^2\right) \tag{5}$$

where q_s is the theoretical isotherm saturation capacity (mg/g); K_{ad} is the Dubinin–Radushkevich isotherm constant (mol^2/kJ^2) and ε is the Dubinin–Radushkevich isotherm constant. The approach was usually applied to distinguish the physical and chemical adsorption of metal ions with its mean free energy y, E per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity) can be calculated by the equation (Dubinin 1960; Hobson 1963)

$$E = \left[\frac{1}{\sqrt{2B_{DR}}}\right] \tag{6}$$

where B_{DR} is denoted as the isotherm constant. Meanwhile, the parameter ε can be evaluated as

$$\varepsilon = RT \ln\left[1 + \frac{1}{C_e}\right] \tag{7}$$

where R, T and C_e represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate

equilibrium concentration (mg/L), respectively. The Dubinin–Radushkevich (DRK) isotherm model is temperature dependent, in which adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed the square of potential energy, all suitable data will lie on the same curve, named as the characteristic curve (Foo and Hameed 2010). Equation (7) is linearized to Eq. (8) which is used in the plot of DRK graph. The constant such as q_s, and K_{ad} were determined from the appropriate plot using Eq. (8) above.

Adsorption kinetics

Adsorption kinetics are very essential in determining the efficiency of adsorption process and adsorbate uptake rate, which in turn controls the residence time at the solid–solution interface. Therefore, it is important to predict the absorption rate for the removal of color from wastewater effluents to design an effluent treatment reactor (Khaled et al. 2009). Two kinetic models, namely, pseudo first order equation and pseudo second order equations were applied for the adsorption of dyes onto calcined eggshell powder.

Pseudo first order kinetics

The pseudo-first-order kinetic model was used to predict the dye sorption kinetics. Pseudo first order equation is given by Ho (2006)

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1}{2.303}t \tag{8}$$

where q_e and q_t are the amounts (mol/g) adsorbed at equilibrium and at time t, and k_1 is the pseudo first order rate constant (min^{-1}). The rate constant k_1 and Q_e can be calculated from the slope and intercepts of $\log (Q_e - Q_t)$ against t. If the calculated Q_e value is equal to the experimental Q_e then the adsorption is following the pseudo first order kinetics (Selvam et al. 2008; Wang and Zhu 2006).

Pseudo second order kinetics

If the rate of adsorption follows the pseudo second order mechanism, then pseudo second order chemisorption kinetic rate equation is expressed as follows (Ho 2006; Ho and Mckay 1998).

$$\frac{t}{Q_t} = \frac{1}{k_2} + \frac{1}{Q_e}t. \tag{9}$$

If the pseudo second order kinetic equation is applicable, then the plot of t/qt versus t should give a straight line, from which q_e and k_2 can be obtained from the slope and intercepts of the plot. The initial adsorption rate is expressed by equation (Aliabadi et al. 2012).

$$h = k_2 q_e^2 \qquad (10)$$

where h is initial sorption rate,

Results and discussion

FT-IR spectroscopy

The FT-IR spectrum is recorded on Shimadzu, 8400-S. FT-IR spectrometer in the range of 4000–400 cm^{-1}. Figure 1 depicts FT-IR spectrum (4000–400 cm^{-1}) for eggshell powder. The absorption peaks observed at 2515.18, 1797.66, 1411.89, 871.82 and 709.80 cm^{-1} confirms presence of CaCO$_3$. The peaks at 3332.99 and 1658.78 cm^{-1} are due to N–H and C=O stretching in the eggshell powder (Guru and Dash 2012).

X-ray diffraction studies (XRD)

X-ray diffraction pattern of the calcined eggshell powder is shown in Fig. 2. The XRD-pattern obtained shows diffraction peaks obtained are characteristics of calcite (CaCO$_3$). Calcite is the thermodynamically most stable form of CaCO$_3$ at room temperature (Islam et al. 2011). The (hkl) plane obtained from XRD-pattern are shown in Fig. 2. The XRD-pattern obtained well matches with JCPDS data (card no. 47-1743).

Crystal morphology

Morphological analysis of calcined eggshell powder performed by SEM is shown in Fig. 3. Figure 3 illustrates SEM images of the calcined eggshell powder as observed, the average diameter in size of the eggshell powder particles was 5 μm. Figure 4 illustrates the EDAX analysis of the eggshell powder. As shown in Fig. 4, the analyzed eggshell powder was composed of the elements calcium

(Ca), oxygen (O), magnesium (Mg), carbon (C) and others. The peaks confirmed that the main component of the eggshell powder was calcium carbonate (CaCO$_3$). The SEM analysis was helpful to determine the surface morphology of an adsorbent. The agglomerate, non-adhesive, porous and irregular surface structure of the adsorbent is distinctly observed in the SEM image.

Thermogravimetric analysis

The thermogravimetric analysis of calcined eggshell powder was measured using a DTG-60 (SHIMADZU) as shown in Fig. 5. Eggshell powder was tested at a heating rate of 20 °C/min from 30 to 800 °C under nitrogen gas flow. The decomposition temperature of eggshell powder is 776.33 °C and it loses the weight nearly 43.397%.

Effect of initial concentration

The Effect of initial concentration on adsorption of Rhodamine B, Eriochrome black T and Murexide dyes onto eggshell powder was determined by keeping adsorbent dose constant. In this study, the adsorption of these dyes was studied by varying concentration range from 1 to 10 mg/L (Thilagavathi et al. 2014). The Fig. 6 shows effect of initial concentration on adsorption of Rhodamine B, Eriochrome black T and Murexide by calcined eggshell powder. This shows that adsorption decreases with increase in concentration of dyes. It was found that adsorption increases rapidly in the beginning and after that it decreases slowly (Subbareddy et al. 2012). In comparison with three dyes, Eriochrome black T shows more adsorption as compared to Rhodamine. This is because when the structure of Rhodamine B and Eriochrome black-T are compared, the former structure is bulkier than latter. Eriochrome black-T exists in sodium salt form, which ionizes in aqueous medium. Therefore, it is more adsorbed in comparison with Rhodamine B dye and Murexide.
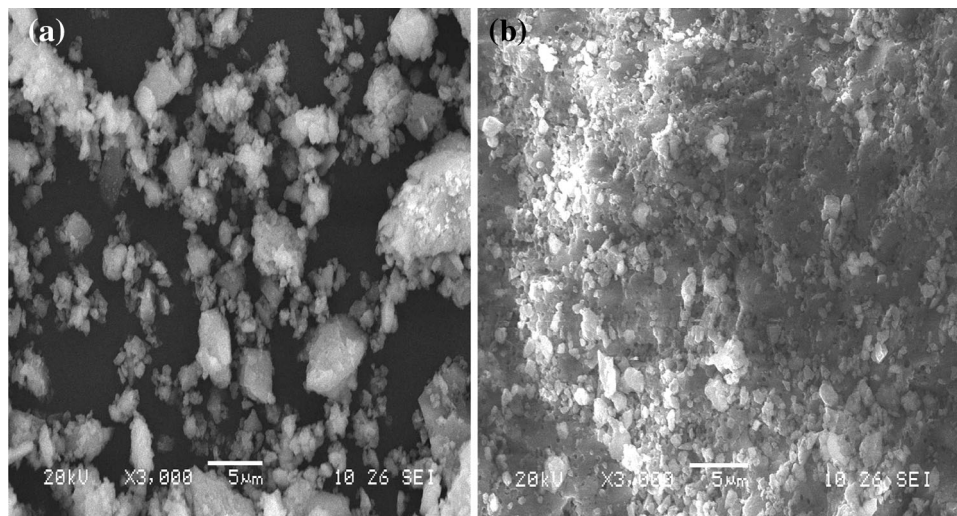
Fig. 1 IR spectrum of calcined eggshell powder
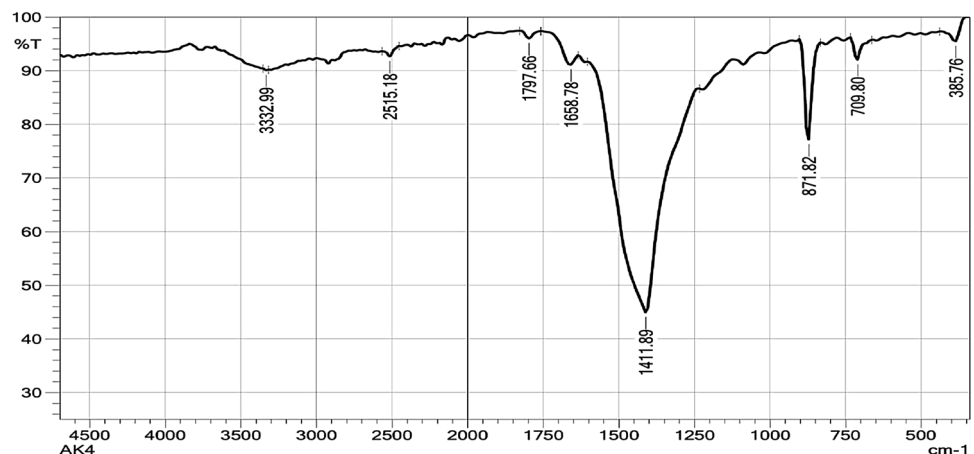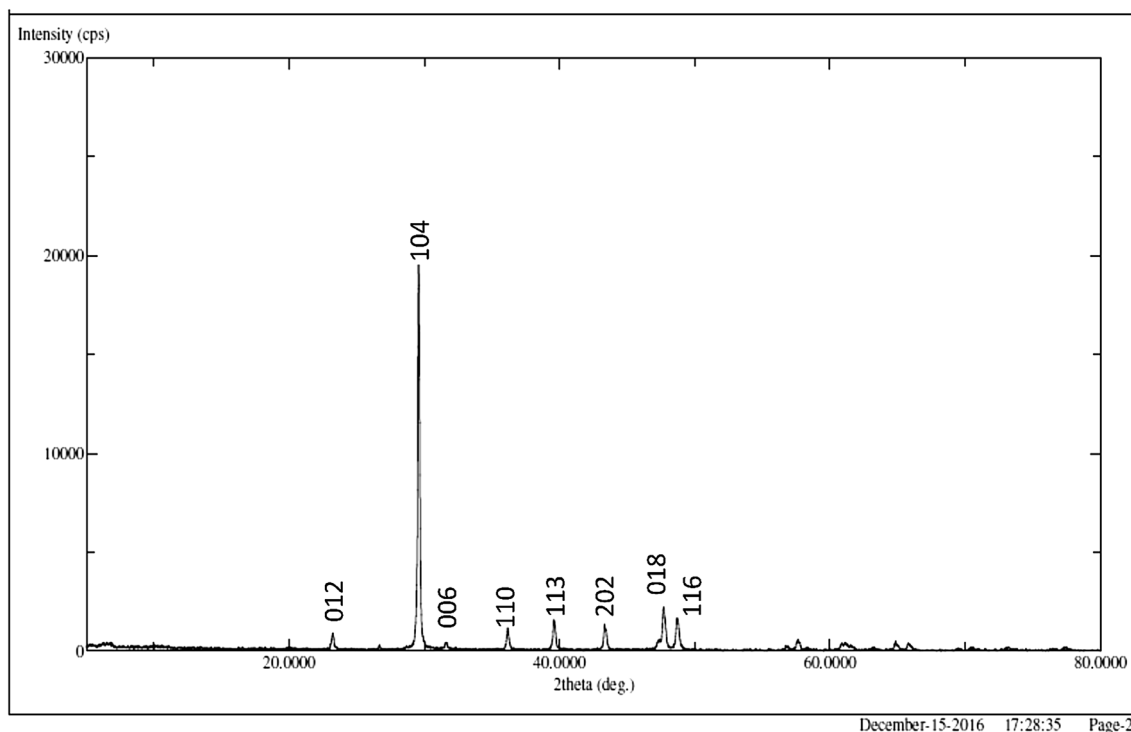
Fig. 2 XRD analysis of calcined eggshell powder

Fig. 3 SEM picture for calcined eggshell powder **a** before **b** after dye adsorption

Second, the structure of Eriochrome black-T is linear as compared to Rhodamine B and Murexide.

Effect of pH

The pH of solution plays an important role for the removal of dyes from their aqueous solution. The Rhodamine B, Eriochrome black T and Murexide dye removal was investigated by varying pH from 1 to 13 (Bernal and McGrath 1994) with an adsorbent dose of 0.250 g, initial concentration 2 mg/L and contact time 2 h as shown in Fig. 7. The

percentage removal of Rhodamine B, Eriochrome black T and Murexide dyes decreased as pH increase from 1 to 13. It was observed that dyes binding adsorbent was pH dependent and the maximum adsorption of dyes to adsorbent was found at pH 5.0 (Haddad et al. 2012).

Effect of adsorbent dose

The Effect of adsorbent dose on adsorption of Rhodamine B, Eriochrome black T and Murexide onto calcined eggshell powder was determined by keeping initial concentration

Fig. 4 EDAX analysis of calcined eggshell powder
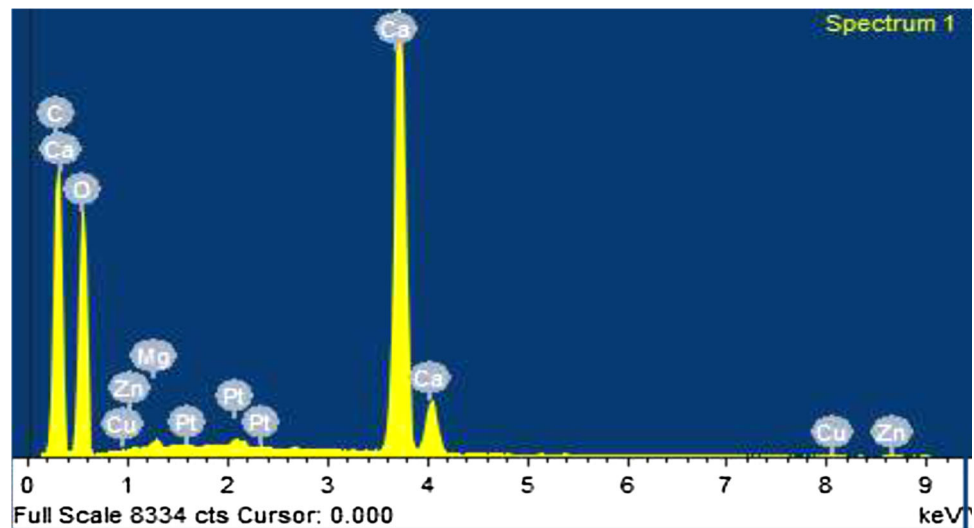
Fig. 5 Thermogravimetric analysis (TGA) graph for calcined eggshell powder
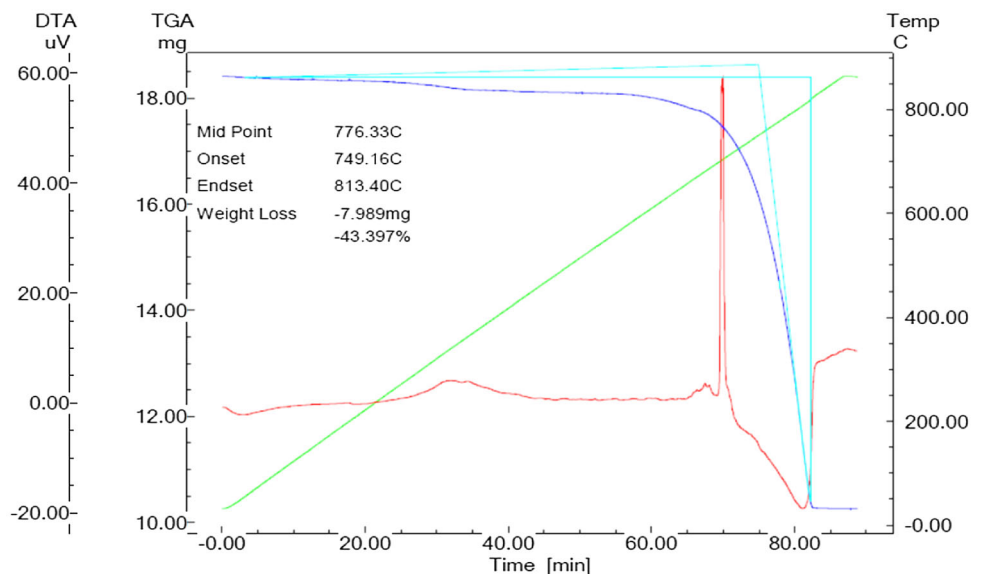
constant. In this study, the adsorption of Rhodamine B, Eriochrome black T and Murexide dyes was determined by varying adsorbent dosage from 0.2 to 2 g. The adsorption process was carried out for 2 mg/L dyes concentration at pH 5.0 (Thilagavathi et al. 2014). Figure 8 shows effect of adsorbent dosage on adsorption of Rhodamine B, Eriochrome black T and Murexide by eggshell powder. This shows that adsorption increases with increase in adsorbent dose. It was found that adsorption increases rapidly in the beginning and after that it increases slowly (Subbareddy et al. 2012).

Effect of contact time

The effect of contact time on adsorption of Rhodamine B, Eriochrome black T and Murexide dyes onto calcined eggshell powder was determined by keeping initial concentration, adsorbent dose constant. In this study, the

adsorption process of Rhodamine B, Eriochrome black T and Murexide dyes was studied for various time including 1, 10, 20, 30, 40, 50, 60, 70, 80 and 90 min (Thilagavathi et al. 2014). Figure 9 shows effect of contact time on adsorption of Rhodamine B, Eriochrome black T and Murexide dyes by calcined eggshell powder. This shows that adsorption increases with increase in contact time as for adsorption more sites are available. It was found that adsorption increases rapidly in the beginning and after that it remains constant. The equilibrium time was found to be 90 min for 2 mg/L dyes concentration at pH 5.0 (Ahlam et al. 2014).

Adsorption isotherms

The Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms were used to measure the

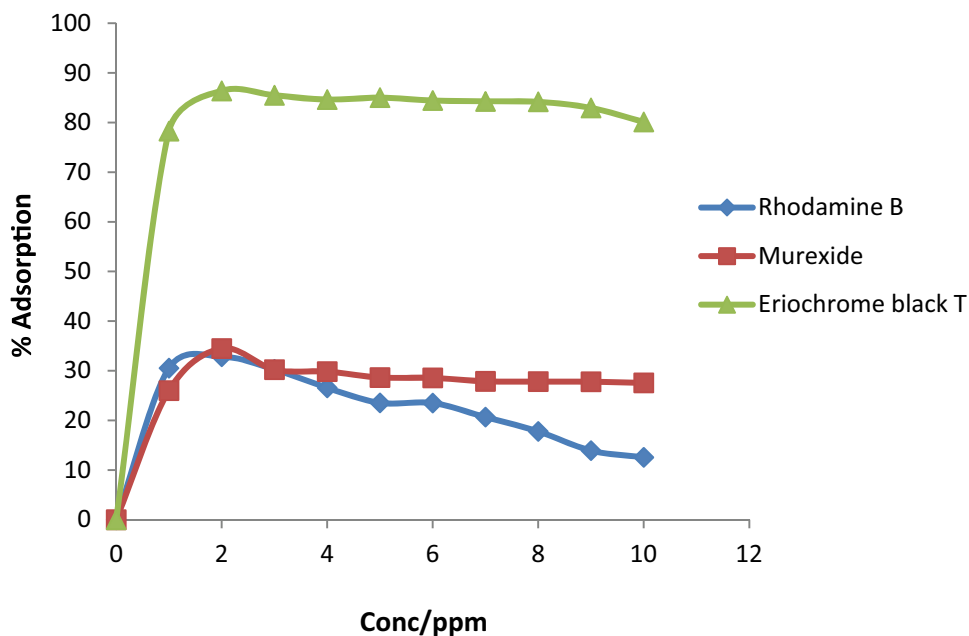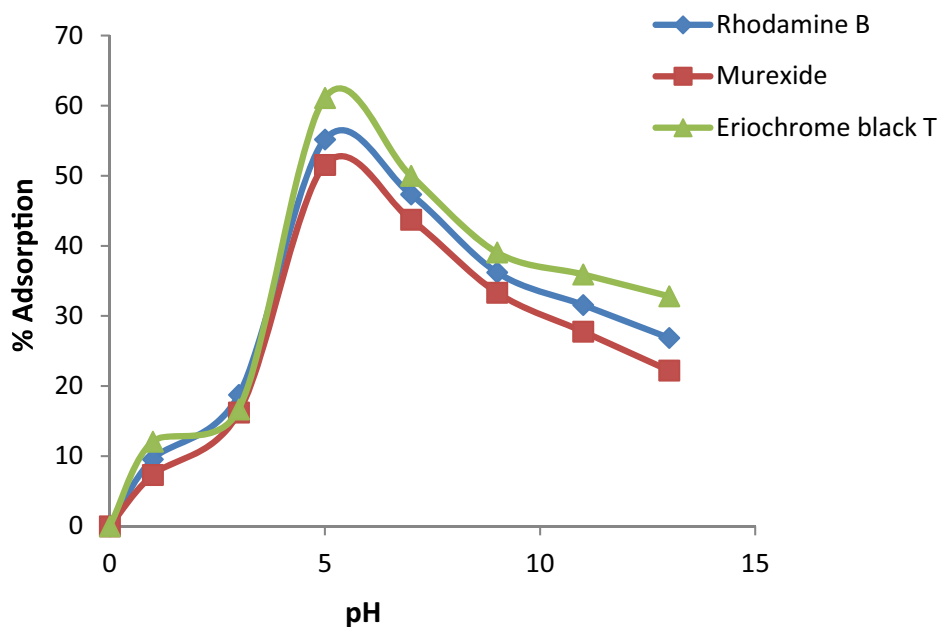**Fig. 6** Effect of initial concentration on dyes

Fig. 7 Effect of pH on dyes

adsorption capacity of calcined eggshell powder for the removal of Rhodamine B, Eriochrome black T and Murexide (Thilagavathi et al. 2014).

Langmuir isotherm

Figure 10 shows Langmuir plot for adsorption of Rhodamine B, Eriochrome black T and Murexide dyes on calcined eggshell powder, respectively. Q_0, K_L and R_L were calculated using Eqs. (1) and (2). Table 2a shows that

R^2 values obtained for Rhodamine B, Eriochrome black T and Murexide dyes onto calcined eggshell powder are in between 0 and 1 indicating that Langmuir isotherm is favourable for all the dyes onto calcined eggshell powder. The Q_0 values obtained for Rhodamine B, Eriochrome black T and Murexide are 1.99601, 1.56494 and 1.03092 (mg g^{-1}). Also by applying linear form of Langmuir equation, the mean of correlation factor R^2 value is found to be 0.9836 this reveal that adsorption data obtained best fits to Langmuir model.
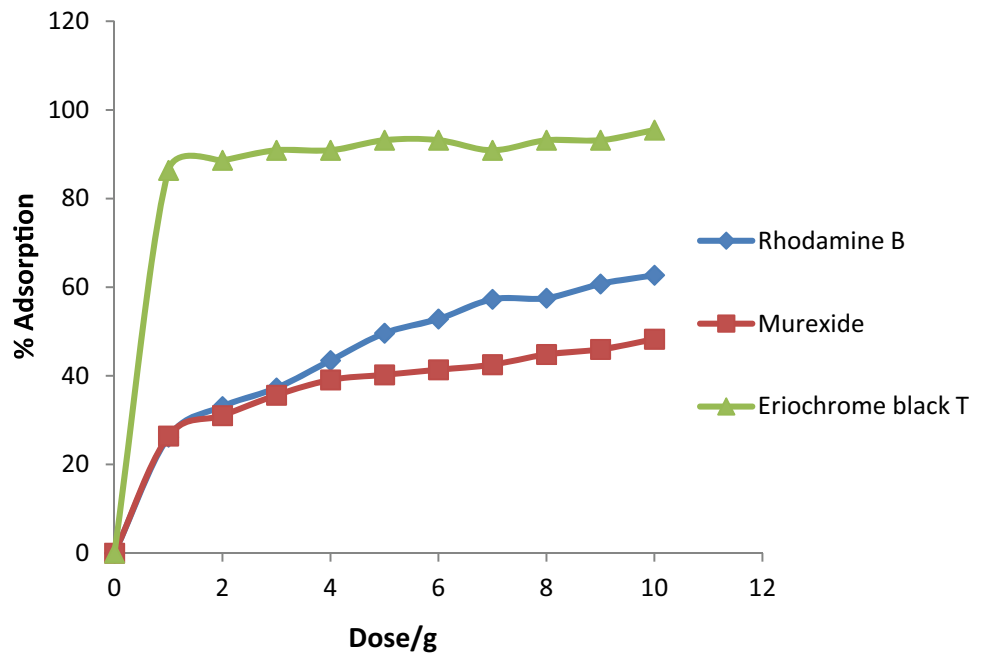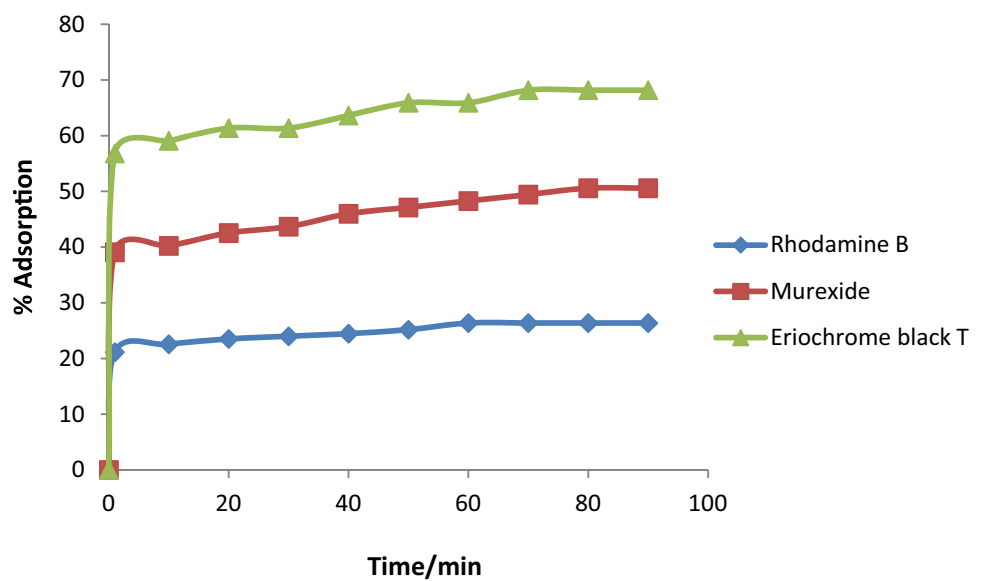
Fig. 8 Effect of adsorbent dose on dyes

Fig. 9 Effect of contact time on dyes

Freundlich isotherm

Freundlich adsorption isotherm depicts Fig. 11 and corresponding data is presented in Table 2a. Adsorption of Rhodamine B, Eriochrome black T and Murexide dyes in aqueous medium onto calcined eggshell powder was successfully investigated using Freundlich isotherm model and corresponding values of K_f and n are calculated using Eq. (3). The constant K_f indicate the adsorption capacity, while the adsorption strength during adsorption process (Voudrias et al. 2002) is measured in terms of $1/n$. The values of n and K_f obtained confirms that adsorption

process (Mohan and Karthikeyan 1997) is feasible. Also the mean R^2 value obtained is 0.9403. The value of n are smaller than 1, hence the process of adsorption is exothermic.

Temkin isotherm

The applicability of this model was verified for adsorption of Rhodamine B, Eriochrome black T and Murexide dyes onto calcined eggshell powder and is depicted in Fig. 12 and the data obtained are presented in Table 2b. B value is calculated using Eq. (4). The plot between the graph Q_e

Fig. 10 Langmuir isotherms plot for adsorption of dyes onto calcined eggshell powder
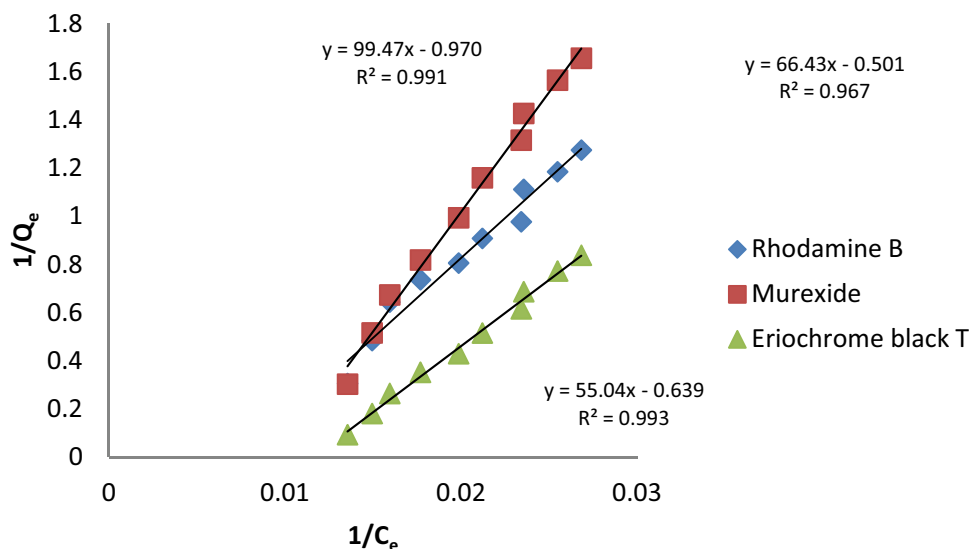

Table 2 Langmuir and Freundlich adsorption isotherm parameters for the removal of Rhodamine B, Eriochrome black T and Murexide by calcined eggshell powder

Dye	T (K)	Langmuir				Freundlich		
		K_L	Q_0 (mg g^{-1})	R^2	R_L	n	K_f (mg g^{-1})	R^2
Rhodamine B	303.15	0.00754	1.99601	0.967	0.3630	0.55524	0.002138	0.921
Murexide	303.15	0.009752	1.03092	0.991	0.3361	0.4432	0.0001538	0.947
Eriochrome black T	303.15	0.01161	1.56494	0.993	0.3163	0.2196	1.965169	0.953

T temperature, Q_0 maximum adsorption amount, m slope, y intercept, K_L Langmuir constant, R^2 correlation factor, n adsorption intensity, K_f Freundlich isotherm constant

Fig. 11 Freundlich isotherms plot for adsorption of dyes onto calcined eggshell powder
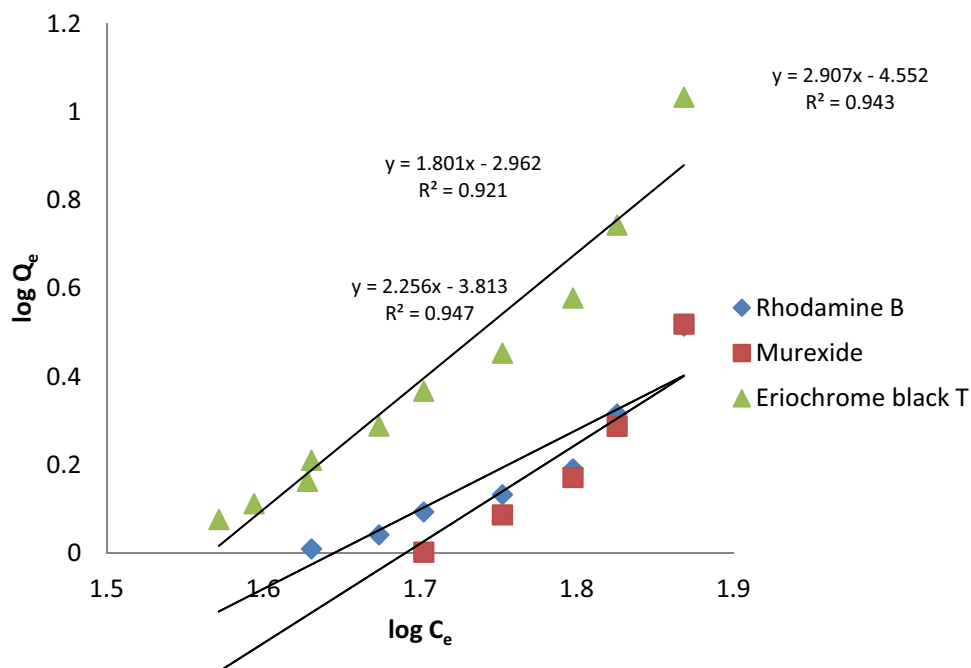
Fig. 12 Temkin isotherms plot for adsorption of dyes onto calcined eggshell powder
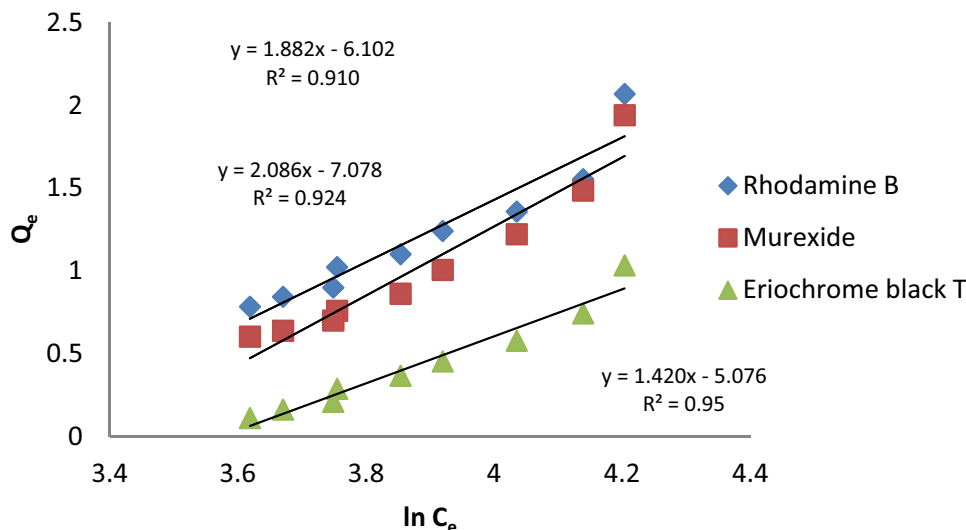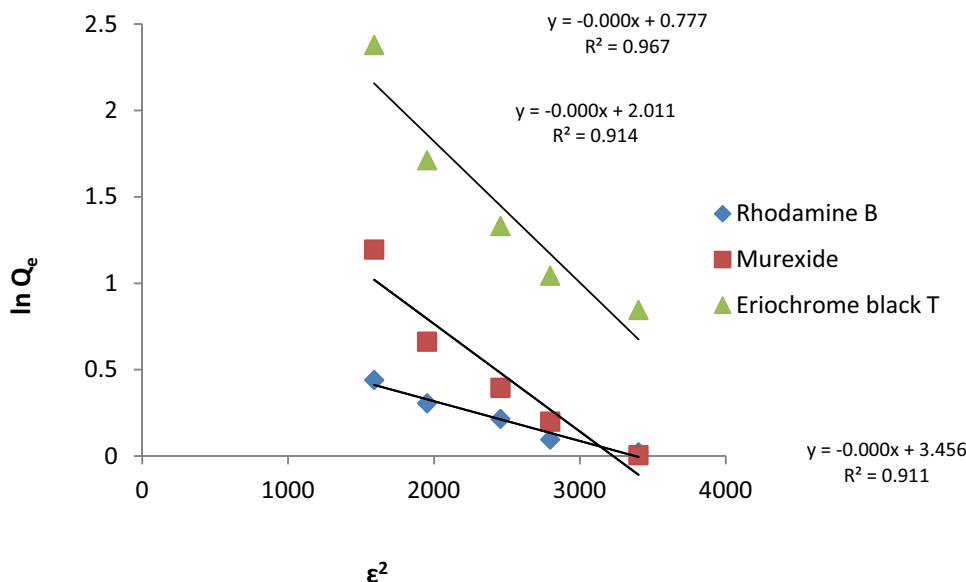
$y = 1.882x - 6.102$
$R^2 = 0.910$

$y = 2.086x - 7.078$
$R^2 = 0.924$

$y = 1.420x - 5.076$
$R^2 = 0.95$

◆ Rhodamine B
■ Murexide
▲ Eriochrome black T

Fig. 13 Dubinin–Radushkevich isotherms plot for adsorption of dyes onto calcined eggshell powder

$y = -0.000x + 0.777$
$R^2 = 0.967$

$y = -0.000x + 2.011$
$R^2 = 0.914$

◆ Rhodamine B
■ Murexide
▲ Eriochrome black T

$y = -0.000x + 3.456$
$R^2 = 0.911$

versus ln C_e gives the slope $= B$, the small value of B (J mol^{-1}) indicates physical sorption and larger value indicates chemical sorption. B value obtained for adsorption are 1.882, 1.42, 2.086, respectively. All these values are small; therefore, they indicate physical sorption. Also the mean of correlation factor R^2 value is 0.928.

Dubinin–Radushkevich isotherm

The adsorption of Rhodamine B, Eriochrome black T and Murexide dyes onto calcined eggshell powder was checked using Dubinin–Radushkevich model and results obtained are depicted in Fig. 13. E and Q_S values are calculated using Eqs. (5) and (6). The plot between ln Q_e versus ε^2, gives the slope $= B$ (J mol^{-1}), the small value of E (0.777, 3.456, 2.011) giving evidence for physical sorption. The

average R^2 value for this model is found to be 0.9306 (Table 3).

Kinetic study

To study the adsorption of Rhodamine B, Eriochrome black T and Murexide dyes using calcined eggshell powder, various kinetic models including pseudo-first and second order were used (Eqs. 8, 9). For adsorption kinetics 0.250 g of calcined eggshell powder was mixed with 50 mL of dyes solution at the initial pH 5 with room temperature (303 K). The mixture was shaken after every time intervals (10 min). The amount of dyes adsorbed at time t, was calculated from the following equation.

$$\text{Amount adsorbed } (Q_t) = (C_o - C_t) \times \frac{V}{m}$$

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Table 3 Temkin and Dubinin–Radushkevich adsorption isotherm parameters for the removal of Rhodamine B, Eriochrome black T and Murexide by calcined eggshell powder

Dye	T (K)	Temkin					Dubinin–Radushkevich				
		B (J mol^{-1})	y	A_T (L g^{-1})	B_T	R^2	K_{ad} (mol^2/kJ^2)	y	E (kJ mol^{-1})	Q_s (mg g^{-1})	R^{2*}
Rhodamine B	303.15	1.882	6.102	0.039074	1321.537	0.910	−0.000	2.3447	0.777	2.174938	0.967
Murexide	303.15	2.086	7.078	0.0336044	1287.9526	0.924	−0.000	1.5999	2.011	7.4707844	0.914
Eriochrome blck T	303.15	1.42	5.076	0.028025	2038.393	0.950	−0.000	2.2772	3.456	31.689963	0.911

T temperature, B constant related to heat of sorption, A_T Temkin isotherm equilibrium binding constant, B_T Temkin isotherm constant, K_{ad} Dubinin–Radushkevich isotherm constant, y intercept, Q_s theoretical isotherm saturation capacity, R^2 correlation factor

Table 4 Kinetic parameter calculated by applying pseudo-first-order and pseudo-second-order for the adsorption of Rhodamine B, Eriochrome black T and Murexide onto calcined eggshell powder

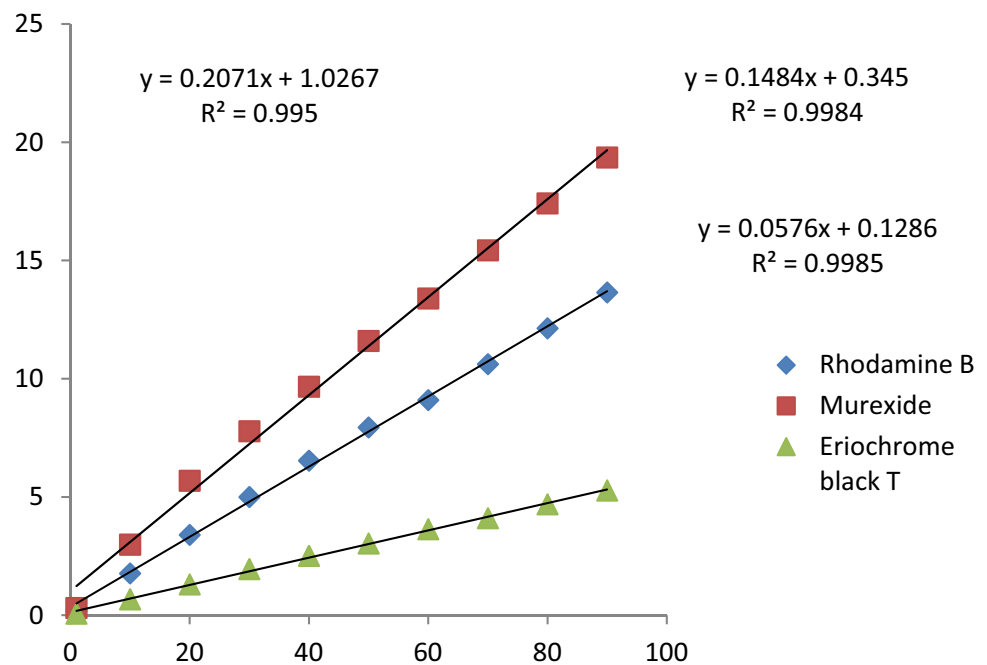| dye	T (K)	Pseudo-first order				Pseudo-second order			
		Q_e (expt) (mg g^{-1})	Q_e (Cal.) (mg g^{-1})	k_1 (min^{-1})	R^2	Q_e (expt) (mg g^{-1})	Q_e (Cal.) (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
Rhodamine B	303.15	6.59	0.53	0.9396	0.732	6.59	6.99	0.0320	0.998
Murexide	303.15	12.64	1.303	9.032	0.654	12.64	12.82	0.020	0.995
Eriochrome black T	303.15	17.04	0.133	0.8544	0.559	17.04	24.39	0.2801	0.998

T temperature, Q_e amount adsorbed at equilibrium, k_1 pseudo-first order rate constant, k_2 pseudo-second order rate constant, R^2 correlation factor

Fig. 14 Pseudo first order plot for adsorption of dyes onto calcined eggshell powder
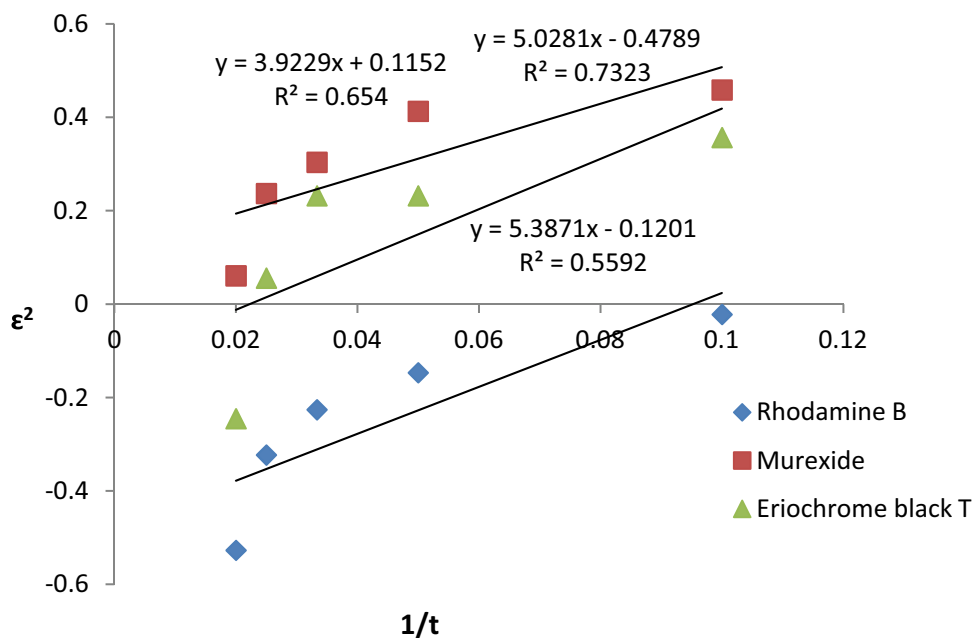
where C_o and C_t (mol/L) are the initial and final concentration at time t of the dye solution, respectively, V (L) is the volume of dye solution and m (g) is the mass of adsorbent used. This shows applicability of kinetic models for Rhodamine B, Eriochrome black T and Murexide and

the experimental data obtained by these models are presented in Table 4. It has been observed from the data, R^2 the correlation coefficient calculated using pseudo second order model was found to be larger 0.997 than those observed for first order model 0.648. Despite the Q_e

Fig. 15 Pseudo second order plot for adsorption of dyes onto calcined eggshell powder

calculated and experimental values evaluated using pseudo first order model (Fig. 14) does not match with each other. On the other hand Q_e calculated and experimental values in case of pseudo second order model (Fig. 15) are in good agreement with each other. Thus, adsorption of Rhodamine B, Eriochrome black T and Murexide dyes onto calcined eggshell powder followed pseudo second order model.

Conclusion

Out of four adsorption isotherm studied Langmuir and Freundlich isotherms were best fitted to the equilibrium data. It confirms that the monolayer adsorption of Rhodamine B, Eriochrome black T and Murexide dyes onto calcined eggshell powder with monolayer adsorption capacity of 2 mg/L. The adsorption kinetics of dyes with calcined eggshell powder did not obey pseudo first order kinetics because the calculated q_e obtained from graph log (Q_e-Q_t) versus t and experimental values of Q_e were not equal. The adsorption kinetics of dyes with calcined eggshell powder obeyed the pseudo second order because calculated Q_e obtained from the graph t/Q_t versus t and experimental values of Q_e were equal. The result of the present study shows that the calcined eggshell powder could be utilized as a cost-effective adsorbent for the removal of dyes.

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