pH Controlled Reversible Interaction of Remazol Orange with Chitin

Muhammad Mominur Rahman[a], Abdullah Muhammad Zakaria[b], Shaikat Chandra Dey[c], Md. Ashaduzzaman[d], Sayed Md. Shamsuddin[e]*

Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering
and Technology, University of Dhaka, Dhaka-1000, Bangladesh

E-mail: [a]mominurrahman007@yahoo.com, [b]abdullahmuhammadzakaria@gmail.com,
[c]shaikat@du.ac.bd, [d]azaman01@du.ac.bd

*Corresponding Author (E-mail: [e]sdin@du.ac.bd)

Abstract. Biomaterials offer alternative opportunities to build sustainable environment compared to synthetic polymeric materials. Here, we utilized a naturally occurring and plentiful biopolymer, chitin, for the studies on interactive phenomena of a reactive textile dye, Remazol Orange (RO), from aqueous solution. The functional groups and crystallinity of chitin were examined by Fourier transform infrared spectroscopy (FT-IR) and x-ray diffraction (XRD) study. Scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) were employed for the exploration of morphology and thermal stability of chitin. In order to investigate the effects of pH, contact time and initial RO concentration, batch studies were performed at room temperature of 25°C. Chitin exhibited a highly pH controlled reversible interaction with RO. RO was bounded 116.3 milligram per gram of chitin at pH 2.0 within 90 minutes of continuous shaking whereas 98.45% (w/w) RO were immediately unbounded from the chitin surface when the in-situ environment was changed at pH 10. Langmuir adsorption isotherm and pseudo-second order kinetic plot indicate homogeneous chemisorption and uniform monolayer of dye molecules on chitin surface. The findings from this study will certainly add value to analytical research leading to advanced applications in separation science and technology.

1. Introduction

Naturally, occurring biopolymers have drawn tremendous attention by many researchers due to their availability, useful properties and numerous industrial applications. The biopolymers are eco-friendly since they undergo gradual biodegradation by available microorganisms after their respective applications. Chitin is the second most abundant biopolymer in nature, next to cellulose [1]. It is relatively inexpensive and readily available resource since several millions tons of chitin are annually harvested in the world. The shell waste of shrimps, prawns, lobsters, crabs and krills are the major commercial sources of chitin, however, it can also be extracted from insects, fungi and other biological materials [2, 3]. Among these sources, shrimp is the most widely available source of chitin. Shrimp processing industries generate large amount of bio-waste which is a rapidly growing environmental concern all over the world [4]. Isolation of chitin from bio-waste of shrimps is an alternative way to minimize environmental pollution. Because of some outstanding properties in terms of environmental concern i.e. biodegradability, biocompatibility, nontoxicity, antibacterial properties, physiological inertness, gel-forming properties, affinity for proteins, particle formation in aqueous solution due to hydrophobic character etc. [5] chitin based materials have already found numerous industrial applications such as adsorbent [6], in affinity chromatography column [7], wound-dressing material [8], enzyme immobilization [5], food industry [5], biosensors [5], binders in the paper making process [9], anticancer drugs [10], excipient and drug carrier in film [11], bone-filling material [11], tissue regeneration [11], applications involving mucoadhesivity [11] etc.

Various methods have been widely employed for the treatment of dyes from the waste water, however, adsorption has been considered as the effective and superior technique [12, 13]. The most widely used adsorbent i.e. activated carbon is costly and is difficult to be regenerated after

adsorption. That is why it is necessary to explore cost-effective and alternative adsorbent materials [14, 15]. The biopolymer chitin is a promising adsorbent material in this regard since the effective functional groups, present in chitin, are capable of adsorbing dyestuffs on the surface of the polymer. Many researchers and their groups have focused on the removal of Remazol dyes by developing adsorbent materials. Silva et al. 2016 reported 20.08 mg adsorption of Remazol Yellow GR per gram of Brazilian fibrous clay at pH 2.0 within 240 min at 25°C [16]. Pelosi et al. 2014 reported 60.86 mg uptake of Remazol Brilliant Blue R per gram of macrophyte *Salvinia natans* at pH 1.0 and at 40°C [17]. Handayani et al. 2016 reported 187.28 mg/g adsorption capacity of chitosan-p-t-butylcalix[4]arene for Remazol Yellow FG at pH 4.0 within 135 min [18]. In our recently published article, we reported 313.4 mg/g adsorption capacity of chitosan for Remazol Red at pH 3.0 within 30 min at 25°C [19]. However, to the best of our knowledge, there is no literature report on the adsorption of RO by chitin. Therefore, in this present study, we took an attempt to utilize chitin for the adsorption of RO, an anionic azo dye, widely used in textile industries.

Adsorption of dyes from waste water using different substrates e.g. activated carbon, naturally occurring materials, synthetic polymers, biosorbents, agrowaste materials, industrial wastes etc. have been reported by many researchers, however, in most of these cases, little attention has been paid to the regeneration of dye-loaded adsorbents [20]. A material must display a higher percentage of regeneration efficiency in order to be employed as an effective adsorbent. Dotto et al. 2015 reported five times reusability of ultrasonic surface modified-chitin/sand for fixed bed adsorption of methylene blue. They performed adsorption-elution cycles ten times using 0.3 mol/L HCl solution at the flow rate of 20 mL/min. The bed performance was strongly impaired after five cycles [6].

According to the literature report discussed above, the adsorption of Remazol dyes is highly pH dependent. Based on this fact, we have closely monitored the pH dependent adsorption and desorption nature i.e. reversible interaction of RO with chitin. Besides, we are reporting rapid adsorption of RO on chitin within 90 min at pH 2.0.

2. Experimental

2.1. Materials
In this study, waste prawn shells were utilized as source of chitin which were supplied from a local prawn hatchery of Bangladesh. Purified sodium hydroxide pellets and 35% hydrochloric acid (w/w) were collected from Active Fine Chemicals Limited, Dhaka, Bangladesh. All of these chemicals were used without further purification. The selected dye, RO, was collected from a local textile industry of Bangladesh.

2.2. Methods
Chitin was isolated from the waste prawn shells according to our recently reported article [19]. A three step process was followed for the preparation of chitin i.e. washing the raw prawn shells with hot water at 80°C for 1.5 h, deproteination by 3% (w/v) sodium hydroxide at 80°C for 3 h and finally demineralization with 11% (w/v) hydrochloric acid at 25°C for 3 h. After this step, chitin was obtained which was washed several times to remove residual acid. Chitin was separated by decantation and was dried in the oven (DO-150, Han Yang Scientific Equipment Co. Ltd., Seoul, Korea) at 60°C for 10 h. The dried chitin flakes were ground into powder before adsorption experiment. Fig.1 shortly depicts the images of various stages during the isolation of chitin.

Figure 1. Images of (a) Prawn, (b) Prawn shells, (c) Chitin flakes and (d) Chitin powder.

2.3. Characterization of Chitin

FT-IR spectrum of chitin was recorded on a FT-IR 8400S spectrophotometer (Shimadzu Corporation, Japan) in the wavenumber range of 4000-400 cm^{-1}. XRD pattern of chitin was recorded by an x-ray diffractometer (Ultima IV, Rigaku Corporation, Japan) at room temperature. Cu Kα radiation (λ=0.154 nm), from a broad focus Cu tube operated at 40 kV and 40 mA, was applied to the sample for measurement. The morphology of the sample was analyzed by an analytical scanning electron microscope (JEOL JSM-6490LA, Tokyo, Japan) operated at an accelerating voltage of 20 kV in the back-scattered electron mode. Thermogravimetric analysis of chitin was performed by a thermogravimetric analyzer (TGA-50, Shimadzu Corporation, Japan) with alumina cell under nitrogen atmosphere at the flow rate of 10 mL/min and at the heating rate of 10°C/min.

2.4. Reversible interaction study

Interaction of RO and chitin was investigated in aqueous phase via batch experiments. Erlenmeyer flasks (100 mL) with air tight stoppers were used in each of which 5 mg of chitin was taken. Twenty (20) mL RO solution having different concentrations was added to the flasks. The flasks were shaken at room temperature of 25°C by a shaker operated at 150 rpm. The pH of the solutions was adjusted using 0.1M NaOH and 0.1M HCl. The concentration of RO in the solution was determined by taking absorbance at 495 nm by a UV-Vis spectrophotometer (UV-2100PC, HumanLab Instrument Co., Korea).

The equilibrium adsorption capacity, q_e, was calculated using the following formula:

$$q_e = \frac{(C_o - C_e)\,V}{m} ,$$

where C_o is the initial concentration of RO (mg/L), C_e is the equilibrium concentration of RO (mg/L), m is the weight of chitin used for the adsorption studies (g) and V is the volume of RO solution (L).

After adsorption, the dye-loaded chitin was subjected to alkaline pH at 8, 9 and 10 in order to observe the desorption nature of RO from chitin surface.

3. Results and Discussion

3.1. Characterization

FT-IR spectrum of chitin showed various absorption bands, typical of crystalline polysaccharides, as shown in Fig. 2(a). The peaks at 1658.78 and 1627.92 cm^{-1} are assigned to the amide I whereas the peak at 1562.34 cm^{-1} is assigned for amide II. The absorption band at 894.97 cm^{-1} is the characteristic marker of the C-H deformation of the β-glycosidic bond. The band 1379.10 cm^{-1} is assigned for C-H deformation. A greater number of narrower bands for C-O-C and C-O were also observed in the region 1200-900 cm^{-1}. The absorption band at 3452.58 cm^{-1} is assigned to the O-H stretching whereas the peaks at 2889.97 and 2927.94 cm^{-1} are assigned to the symmetric and asymmetric stretching vibration of C-H [21].

Fig. 2(b) shows the diffractogram of chitin. The XRD pattern of chitin showed a characteristic diffraction peak at 2θ around 19.27°. The crystalline index (CI) was calculated from the XRD pattern as follows [22]:

$$\text{CI Value} = \frac{(I_{110} - I_{am})}{I_{110}} \times 100 ,$$

where I_{110} is the maximum intensity of the diffraction at 19.27° and I_{am} is the intensity of amorphous diffraction at 12.77°. The calculated CI value from this equation is 96.16% which falls in line with many other CI values of chitin reported in literature. Liu et al. 2012 reported 89.17% crystalline index for shrimp chitin [23].
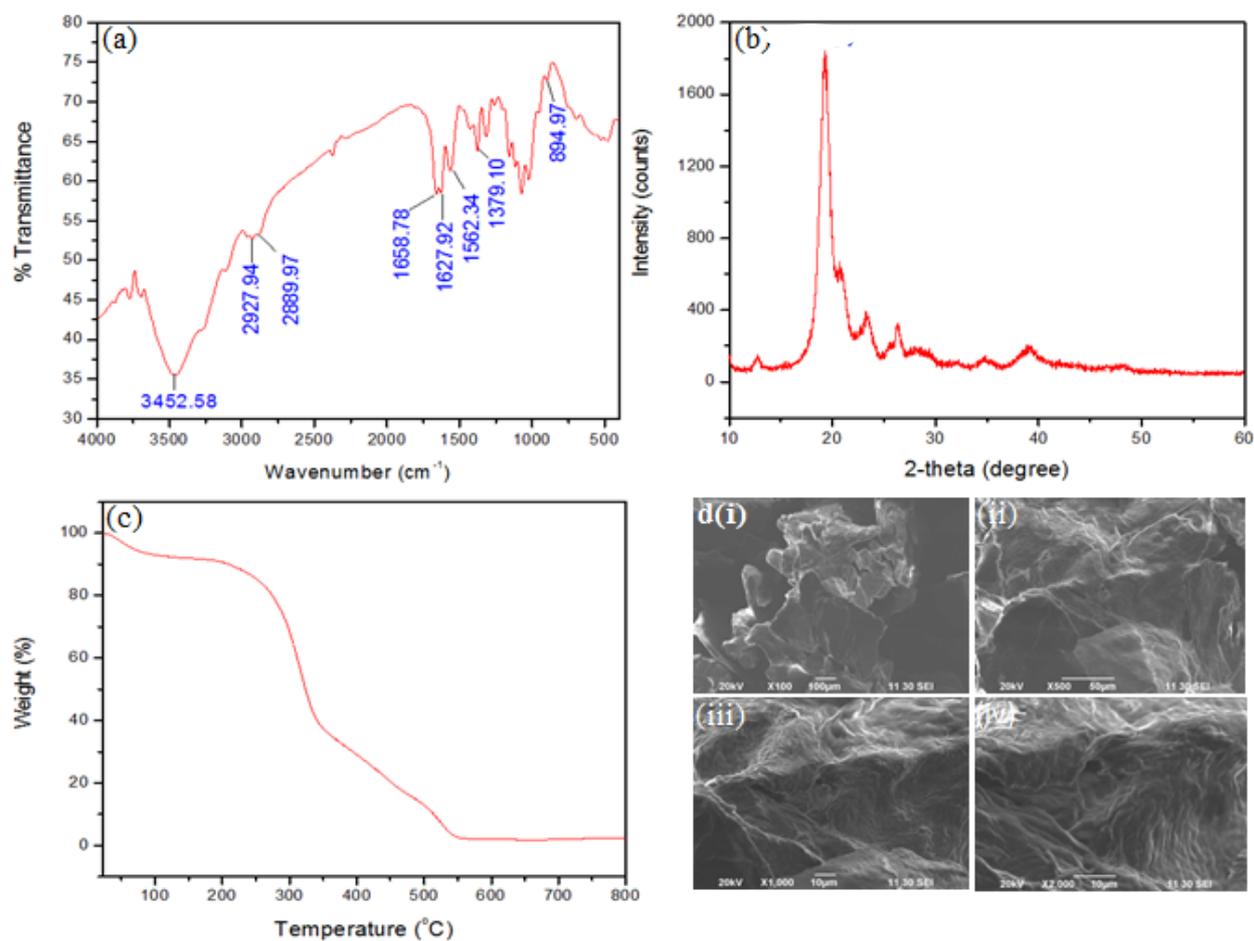
Figure 2. (a)FT-IR spectrum, (b)XRD pattern, (c)TGA thermogram and (d)SEM microphotographs of chitin at different magnifications.

The thermal degradation profile of chitin is well understood from its TGA thermogram as depicted in Fig. 2(c). In this thermogram, there are two weight loss steps. The first weight loss step (0-200°C) is attributed to the evaporation of moisture from its structure whereas the second weight loss step (200-550°C) indicates the decomposition of chitin [24].

The morphological feature of chitin is well illustrated by SEM micrographs as presented in Fig. 2(d). The micrographs showed rough and non-homogeneous surface without porosity which might be attributed to their high molecular packing, with inter or intra molecular hydrogen bonds, imparting a high crystalline degree to chitin [22]. The surface was observed to be fibrous with increase in zooming especially at X2000 magnification which is clearly shown in Fig. 2(d. iv). [25].

3.2. Literature Review

Chitin has been regarded as a potential adsorbent material for the removal of various types of pollutants from industrial effluents. The removal of dyes, heavy metals and surfactants by chitin based materials has been immensely reported in literature which is briefly summarized in Table 1.

Table 1. Chitin based materials as adsorbent for different types of pollutants.

Pollutant Type	Name of Pollutant
Dyes	Acid Blue 25, Acid Blue 158, Mordant Yellow 5 and Direct Red 84 [26]; Yellow D-5GN, Red D-8B, Ruby F-2B, Blue D-5RN, Black DN, Yellow 2R, Scarlet R, Gelb GR, Brilliant Orange 3R and Blau 3R [27]; Reactive Red 141 [28]; Black DN [29]; Yellow D-5GN, Red D-8B, Blue D-5RN, Black DN, Ruby E-2B, Yellow 2R, Scarlet R, Gelb GR, Brilliant Orange 3R, Blau 3R [30]; Scarlet R, Brilliant Orange 3R, Black DN [31, 32]; Ponceau-S [33]; Indigo Carmine [34]; Reactive Yellow 2, Reactive Black 5 [35]; Methylene Blue [6, 36]; Neoland Blue 2G, Eriochrome Flavine A and Solophenyl Brown 3RL [37]; Malachite Green [38]; Verofix Red [39]; FD&C Red No. 40 [40]
Heavy Metals	Zn (II) [41, 42]; Cr (III) [43]; As [44]; Cd (II), Ni (II) [45]; U [46]; Pb (II), Cd (II) and Cu (II) [47]; Pb (II), Cd (II) and Co (II) [48]; Actinide [49]; Cd (II) [50]; Silver-Thiosulphate [51]; Cu (II) and Ni (II) [52]; Fe (II) and Mn (II) [53]; Al (III) [54]
Surfactants	Borutosol KRN, Siarczanol N-2 and Rokafenol N-8 [31]; Borutosol KRN, Siarczanol N-2 and Rokafenol N-8 [55]

3.3. Effect of experimental conditions on adsorption performance

Fig. 3(a) shows a calibration curve of absorbance vs. concentration, which was plotted for RO using its standard solutions. This curve was utilized for calculating the adsorption capacity with respect to three variables i.e. pH, contact time and initial concentration.

As shown in Fig. 3(b), the adsorption of RO on chitin surface was highly influenced by the solution pH. Chitin contains three functional groups: hydroxyl, amino and amide. In acidic solution, the amino groups of chitin become protonated. As a result, anionic dye molecules are adsorbed onto to the positively charged surface of chitin. According to the figure, the maximum adsorption was observed at pH 2.0. This phenomenon occurred, may be due to the maximum protonation of amino groups at this pH. When the pH was increased above 2.0, adsorption capacity decreased gradually which might occur due to the progressive deprotonation of amino functional groups. When the pH was decreased below 2.0, adsorption decreased because the azo functional groups of dyes are protonated at lower pH [56]. As a result, there is repulsion between the positively charged azo groups and the positive charge on the active sites of chitin which reduced the extent of adsorption. At pH above 7, the rate of adsorption decreased rapidly. This is because in alkaline media, the amine functional groups are no longer protonated and also there is a competition between the hydroxyl ions and anionic dyes for the adsorbent. Therefore, pH 2.0 was selected for the optimization of contact time and concentration.
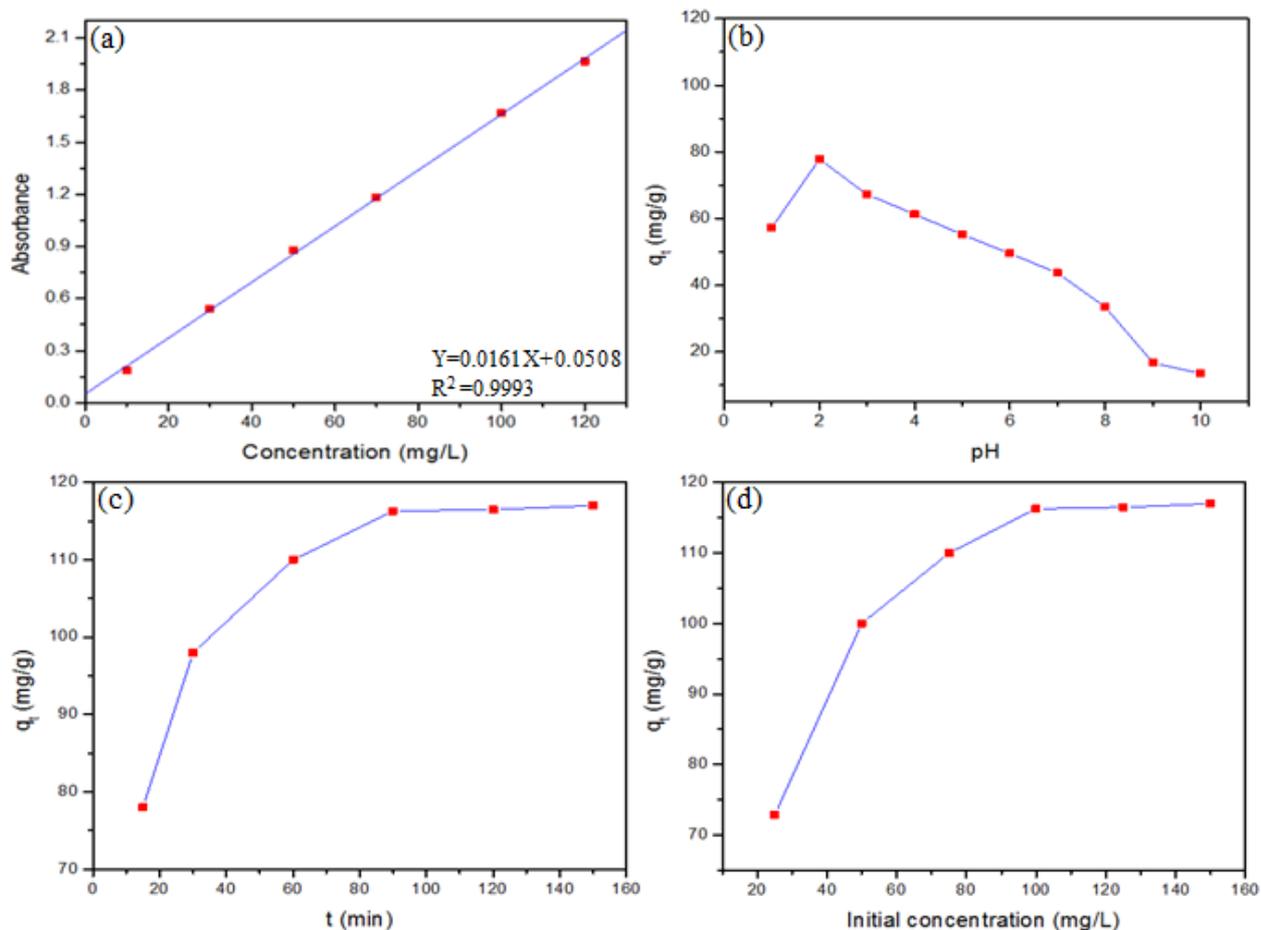
Figure 3. (a) Calibration curve of RO, (b) Effect of pH, (c)Effect of contact time and (d) Effect of initial concentration on the adsorption of RO on chitin.

Contact time played a significant role in the adsorption of RO on chitin as illustrated in Fig. 3(c). The extent of adsorption increased progressively with gradual increase in contact time and after 90 min of continuous shaking, the adsorption process reached equilibrium. Initial rate of adsorption was higher compared to the later stage. Higher number of vacant active sites on the surface contributed to the higher initial rate of adsorption. However, with the passage of time, the vacant sites were gradually covered by the dye molecules. The slow pore diffusion of the dye molecules prevented the remaining active sites from being occupied by the dye molecules [57]. Therefore, contact time of 90 min was selected for optimization of initial RO concentration.

As indicated in Fig. 3(d), the extent of adsorption increased with increase in initial RO concentration. This is because the driving force of adsorption is the concentration gradient which increases with increase in initial dye concentration [58]. The adsorption process reached equilibrium for 100 mg/L RO concentration. Therefore, the adsorption process was optimized under the following condition: pH: 2.0, contact time: 90 min and initial RO concentration:100 mg/L. At this optimized condition, the calculated adsorption capacity was 116.3 mg/g.

3.4. Isotherm and kinetic study

The equilibrium adsorption data were plotted in two well-known isotherm equations as shown in Fig. 4(a) and Fig. 4(b). However, the value of linear regression correlation coefficient i.e. R^2 was found higher from Langmuir isotherm (R^2=0.9938) than Freundlich isotherm (R^2=0.8152). Therefore, equilibrium adsorption data were fitted better in Langmuir adsorption isotherm. The isotherm study confirms that there was a homogeneous and monolayer adsorption of negatively charged RO molecules on the positively charged chitin surface.
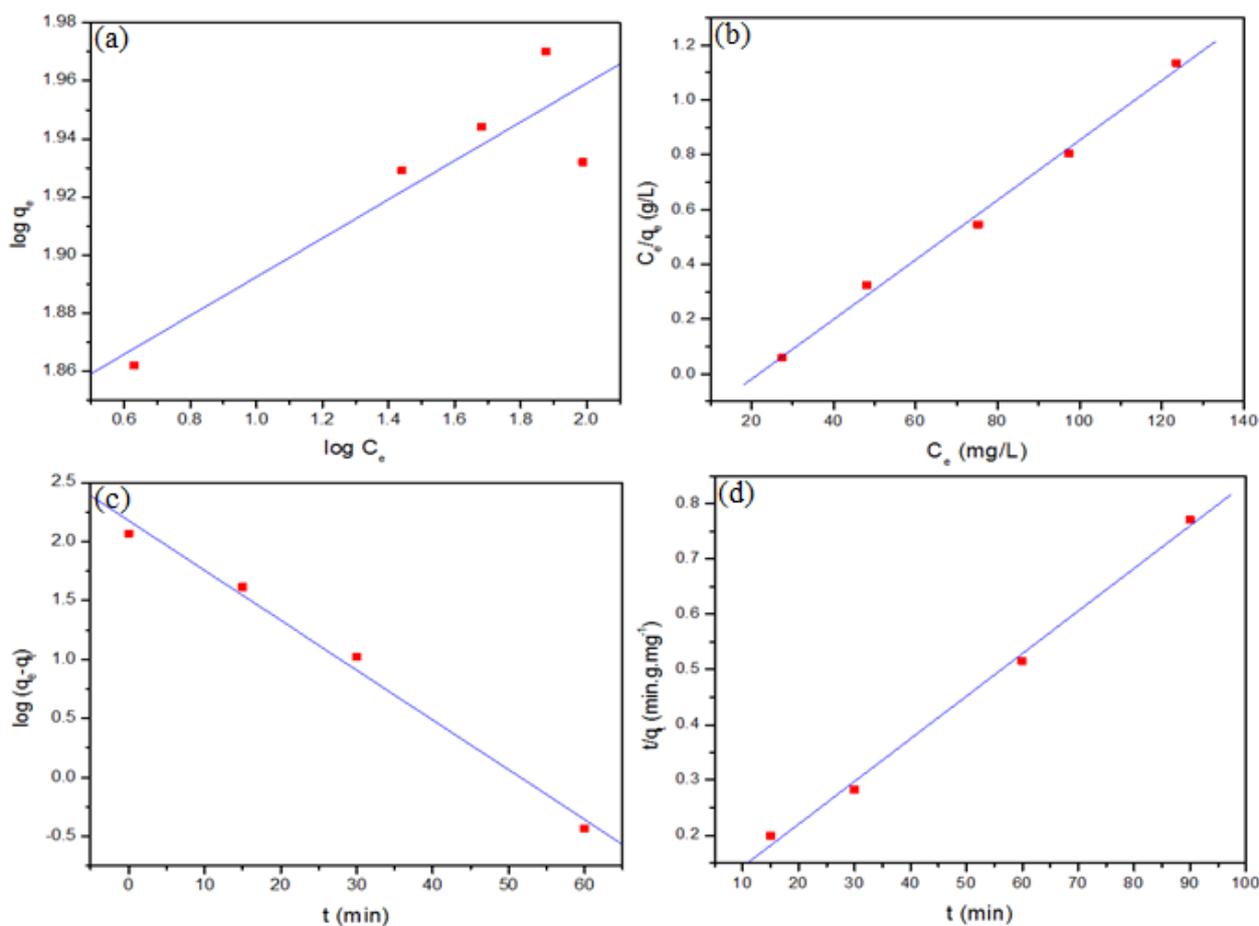
Figure 4. (a) Freundlich isotherm, (b) Langmuir isotherm, (c) Pseudo-first order kinetic plot and (d) Pseudo-second order kinetic plot.

Similarly, the adsorption data were plotted in two kinetic equations as indicated in Fig. 4(c) and Fig. 4(d). However, the value of R^2 was found higher in case of pseudo-second order kinetics (R^2=0.9960) than pseudo-first order kinetics (R^2=0.9897). As a result, it can be concluded from the kinetic study that the negatively charged RO molecules were chemisorbed on the positively charged bio-surface of chitin.

3.5. Mechanistic illustration of reversible interaction

The dye-loaded chitin was subjected to alkaline pH at 8, 9 and 10 successively to observe desorption of RO from chitin surface. It was revealed that liberation of RO from chitin surface occurred immediately after pH adjustment and there was a gradual increase in desorption with increase in pH as displayed in Fig. 5(a). At pH 10.0, 98.45% (w/w) RO were desorbed from chitin surface whereas at pH 2.0, 116.3 milligram of RO was adsorbed per gram of chitin which has already been mentioned earlier in Fig. 3(d). From this observation, it can be concluded that the solution pH played the determining role for the adsorption/desorption of RO on/from chitin surface. Therefore, the aqueous phase interaction between RO and chitin was pH dependent and reversible. The mechanism for reversible interaction between RO and chitin is schematically illustrated in Fig. 5(b) which shows that dye molecules are adsorbed on the chitin surface at pH 2.0 and desorbed from the surface at pH 10.0. Fig. 5(b) also depicts the images of chitin after adsorption and desorption of RO. At pH 2.0, chitin surface was covered by dye molecules and therefore chitin powder displayed the color of RO. However, the actual color of chitin surface was observed at pH 10.0 due to the removal of adsorbed RO from chitin surface.
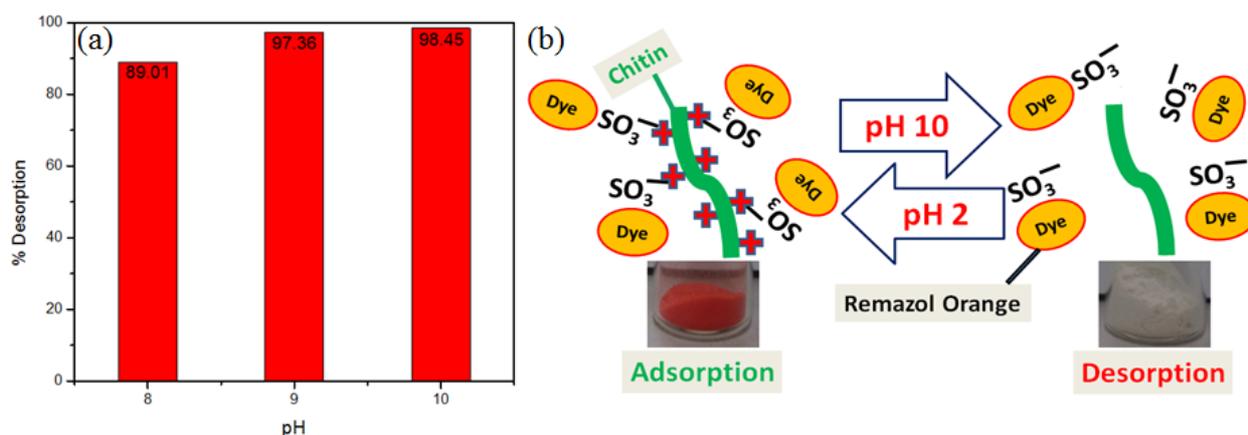
Figure 5. (a) Bar diagram of % Desorption vs. pH and (b) Schematic illustration for the adsorption/desorption mechanism of RO on/from chitin surface (Inset shows the dye-loaded and dye-free chitin powder respectively).

3.6. Interfacial interaction of RO with chitin

It is evident from Fig. 6 that the intensities and positions of a few signals-recorded from chitin-have been altered after dye adsorption. The absorption bands at 1627.92 and 1625.99 cm^{-1} were recorded from chitin and RO respectively. Interestingly, after dye adsorption the peak at 1627.92 cm^{-1} has been shifted to a lower wavenumber of 1625.99 cm^{-1}. From this discussion, it can be concluded that at pH 2.0, RO was electrostatically attached on the positively charged chitin surface.
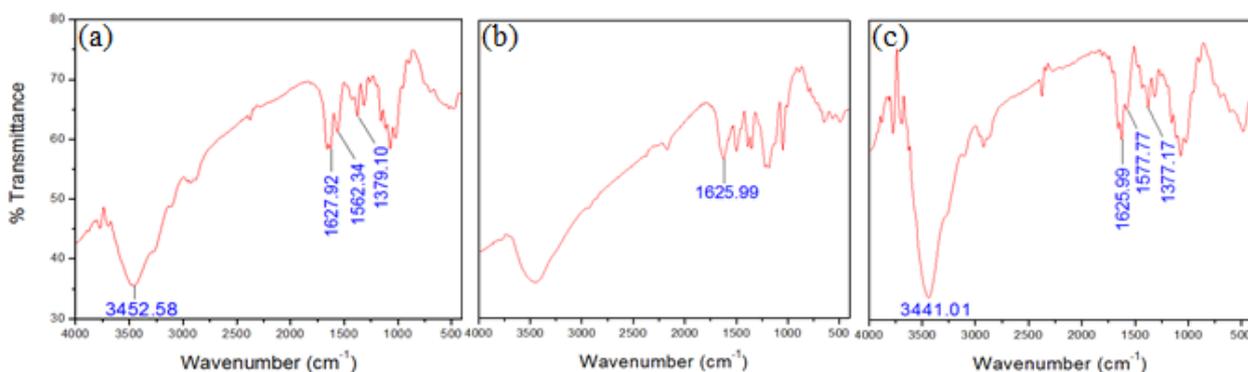

Figure 6. FT-IR spectra of (a) Chitin, (b) RO and (c) Chitin after RO adsorption.

3.7. Specific surface area (SSA) analysis

The positively charged surface of chitin played the vital role for the adsorption of negatively charged RO at pH 2.0. It is established that the smaller size adsorbent with higher surface area exhibits higher degree of adsorption. Powdered phase has higher surface area than packed crystalline state of chitin. In 2016, Dassanayake et al. reported the Brunauer-Emmett-Teller (BET) specific surface area of shrimp shell of 3.12 m^2/g [36] from the N$_2$ adsorption isotherm. The chitin used in the research work was produced via similar technique which implies the size of chitin may be around 3.0 m^2/g.

4. Conclusions

Chitin has drawn tremendous attention from industry due to its outstanding physico-chemical characteristics. Higher adsorption capacity, rlegeneration efficiency, cost-effective and eco-friendly nature of chitin have made it an attractive adsorbent material to be employed for the remediation of environmental hazards from industrial effluents. Chitin showed a very good adsorption capacity of 116.3 mg/g for RO at pH 2.0 and 98.45% (w/w) regeneration at pH 10. The rate of adsorption increased with increase in contact time and initial RO concentration. Equilibrium adsorption data exhibited good correlation with Langmuir adsorption isotherm and pseudo-second order kinetics as

evidenced by the value of linear regression correlation coefficient. Higher adsorption capacity and significant regeneration efficiency are key parameters for an adsorbent material to be applied industrially. Therefore, it can be concluded that chitin has a great potential to remove RO and similar types of anionic azo dyes from industrial effluents.

Acknowledgements

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