Thermochemical Conversion of Waste Glass and Mollusk Shells into an Absorbent Material for Separation of Direct Blue 15 Azo Dye from Industrial Wastewater

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ABSTRACT: The objective of the presented work was to convert waste glass and mollusk shells into a porous material for separation of the direct blue 15 azo dye from industrial wastewater. The porous glass material of specific pore size and surface area was prepared through a thermochemical reaction by reacting waste glass with mollusk shells, soda, and rock salt. The optimal reaction conditions were determined by adjusting the reaction time, reaction temperature, and relative amount of the reactants. The surface morphology, elemental composition, and functional groups of the material were studied through scanning electron microscopy (SEM), X-ray fluorescence spectroscopy (XRF), energy-dispersive X-ray spectroscopy (EDX), and Fourier transform infrared spectroscopy (FT-IR). Barrett–Joyner–Halenda (BJH) and Brunauer–Emmett–Teller (BET) methods were used to determine the pore size distribution and surface area of the porous material. The material consisted of different types of flakes, oval-shaped particles, and granules. In addition to the functionalized char, the porous material contained Si−O−Si, Si−O−Al, and Si−OH groups. Relatively better yield and pore size distribution were obtained at a reaction temperature of 800 °C and reaction time of 90 min. The fully characterized material was used to separate the blue dye from industrial wastewater. This porous material absorbed about 2.66 mg/g blue dye from wastewater after 20 min of treatment time. The adsorption data fit the Freundlich isotherm better than the Langmuir isotherm. The correlation coefficient of Freundlich isotherm varied from 0.93 to 0.98, which was slightly higher than the correlation coefficient of Langmuir isotherm.

1. INTRODUCTION

Glass is a highly stable material due to its vitreous nature and stable silicate backbone. The world produces 2.01 billion tons of solid waste annually, with at least 4−8% glass by weight.1−4 Glass can be recovered from the solid waste in broken and nonbroken forms and sorted into various colors, such as flint, amber, and green. Sorting the waste glass by color increases its market value. The glass containers, beverage bottles, and the glass obtained during demolishing and renovation of buildings are the major sources of solid waste. Glass does not naturally breakdown or degrade over time due to its inert nature and high resistance to degradation. Its chemical nature does not change with a change in outdoor temperature and environment. Repeated recycling of glass is possible without altering its physicochemical properties due to the high stability of silicates. It can also be converted into nonvitreous and porous materials through a suitable thermochemical reaction for separation of pollutants from industrial wastewater. The textile effluents contain different dye pollutants. Owing to high toxicity, these pollutants are detrimental to the environment and human health. Textile dyes significantly degrade the esthetic quality of water bodies; increase the chemical oxygen demand (COD) and biochemical oxygen demand (BOD); inhibit plant growth; impair photosynthesis; result in recalcitrance and bioaccumulation; and promote toxicity in foods, carcinogenicity, and mutagenicity.2−5

Several methods are being used to treat the effluents of textile industry.4−7 One such method is the adsorption of dyes onto clay and other porous materials. Adsorption is a relatively simpler and low-cost method for treatment of textile effluents. The chemically converted glass into a porous material can also be used for adsorption treatment of dye-containing industrial wastewaters. The porous glass is produced through a number of methods, including etching of liquating glass fibers, foaming of

Received: April 13, 2020
Accepted: June 29, 2020
Published: July 13, 2020

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Figure 1. Proposed porous structure and adsorption of direct blue 15 dye onto modified glass having silicate functionalities and char-based nitrogenous and non-nitrogenous functionalities.

Glass melts, sintering of glass powders, blowing of agents, burning of additives, slip technology, matrix duplication, sol–gel method, liqation gel separation, and thermochemical conversion.\(^6\)–\(^8\) Porous glasses can also be produced by changing the glass composition, such as the concentration of zinc oxide, calcium oxide, strontium oxide, magnesium oxide, and barium oxide.\(^7\)–\(^11\) Verné et al.\(^12\) studied the in vitro behavior and reactivity of glass ceramics and bioactive glasses. It was revealed that the thermal properties, surface reactivity, and stability of modified glasses depend on the ratio of modifier oxides and magnesium oxide.\(^12\) Mollusk shells are a low-cost natural source of calcium compounds, such as aragonite and calcite.\(^13\) Aragonite is a crystal of orthorhombic symmetry where calcium is octahedrally nine-fold calcium site is coordinated by oxygen. Calcite is also a crystal of trigonal symmetry where calcium is octahedrally coordinated by oxygen. Mollusk shells can be used as a modifier for converting waste glass into a porous material.\(^14\) The possible reaction between aragonite and calcite compounds of mollusk shells with waste glass and the dye adsorption mechanism are illustrated in Figure 1. The mollusk shells contain biopolymers and biominerals, which react with molten glass and change its structure, viscosity, and chemical composition. The biopolymers decompose at higher reaction temperatures and produce different gases. These gases change the viscosity, melting point, and porosity of the modified glass.

Although the use of shells as biosorbsents has already been documented in the literature for removal of dyes and metal ions from wastewater, the presented work focuses on the use of mollusk shells as a flux.\(^14\)–\(^17\) The shells were used as a flux and modifier for the molten phase devitrification of waste glass. Having high functionalized and crystalline structure, the mollusk shell promotes the in situ formation of properly templated carbon and char moieties during the devitrification reaction. It works as a flux for glass devitrification, template for imprinting the silicate backbone of glass, source of char for enhancing the adsorption capacity of the glass-based adsorbent, and source of porogenic gases and materials.\(^14\)–\(^16\)

The most desired property of materials to be used as separating media is their porous and microporous nature. The interaction of glass with mollusk shells at higher temperatures produces carbon dioxide, oxides of nitrogen, and oxides of the sulfur. The elemental composition of mollusk shells is defined as C, O, H, P, N, S, Ca, and Si and some trace elements.\(^17\)–\(^19\) These elements exist in the form of biopolymers and biominerals. The mollusk shell as a flux induces structurally different properties and composition of porous glass. This flux also adds some char functionalities to the porous glass. When reacted with mollusk shells, the porosity of glass increases due to in situ production of insoluble and non-interacting gases during decomposition of mollusk shells. These gases leave the devitrification reaction by creating pores in the molten glass. If a rock salt is added to the devitrification reaction, it promotes the cracking of vitreous skeleton of glass by solubilizing the glass at higher temperatures.

In this study, a porous glass adsorbent was prepared through the thermochemical reaction of waste glass with mollusk shells, sodium bicarbonate, and rock salt. The thermochemical devitrification of glass was carried out through solubilization, decomposition, and chemical interactions. The important aspect of the study was to reduce the process cost by lowering the reaction temperature. Mollusk shells not only help lowering the reaction temperature but also generate activated carbon to activate the porous sites for adsorption of textile dyes. The direct blue 15 dye with IUPAC name \"2,3,3′-[(3,3′-dimethoxy-4,4′-biphenyl]ylene)bis(azo)]bis[S-amino-4-hydroxy,-tetrasodium salt\" was used as an adsorbate. It is an organic compound \(\text{C}_{34}\text{H}_{24}\text{N}_6\text{O}_{16}\text{S}_4\text{Na}_4\) that is classified as an azo dye of anionic nature.\(^20\),\(^21\) Since the direct blue 15 dye is an anionic salt at high pH values and acidic at lower pH values, its reactivity with the adsorbent varies with the pH value. The dye is adsorbed onto various surfaces through electrostatic interactions. The porous glass offers a number of charged sites for dye adsorption in the
form of silicate functionalities and char-based nitrogenous and non-nitrogenous functionalities. The dye binds to these functionalities by electrostatic forces or bonding forces of NH$_2$ groups in the dye. At lower pH values, the porous glass adsorbs protonated moieties by interacting with NH$_2$, OH, and N=N groups. This adsorption happens mainly through lone pairs associated with the nitrogenous moieties. At higher pH values, the porous glass adsorbs the anionic form of dye through electrostatic forces due to vacant orbitals of Al atoms and the van der Waal’s force sites present in the structural defects, pores, and the molecular holes of the adsorbent.

2. RESULTS AND DISCUSSION

2.1. Effect of Reaction Temperature. The use of mollusk shells as a flux can have a profound impact on the reaction temperature, porous product quality, and product yield. The biopolymers and biominerals in the shells change the structure of calcium compounds, chemical composition, and other properties of the porous product. It is believed that the biopolymers also change the thermal behavior of the waste glass and other reactants. On heating, these biopolymers undergo extensive decomposition and produce large quantities of gases. These gases change the viscosity, vapor pressure, melting point, and boiling point of waste glass mixture. The melting and boiling points reduce while the porosity level increases with an increase in the amount of gases. These changes also affect the chemical composition of the product. The fusion and reaction of molten salt with glass depend on the reaction temperature, which is influenced by the viscosity and type of active species in thermochemically decomposed reactants.

Optimum temperature was found by varying the reaction temperature from 400 to 800 °C for processing of the waste glass into porous product. The experiments on temperature optimization were conducted by combining glass, shells, soda, and salt in a ratio of 3:3:2:2. Results of this study are presented in Table 1. The degree of reaction during thermochemical recycling of waste glass was revealed by measuring the postreaction weight loss. The material loses weight during the thermochemical reaction and dissolution in water. The loss in weight during a thermochemical reaction is attributed to the decomposition reaction and emission of gases. The loss in mass during decomposition of reactants was relatively lower than during dissolution in water. In the presence of mollusk shell flux, the weight loss was gradual and relatively less as compared to that with the lime flux. It might be due to the characteristic nature and structure of the flux and deposition of the char on the glass-based material.

Two types of materials were obtained after thermochemical decomposition of reactants and dissolution in water. The materials were classified into hard material and porous powdered material. Since formation of a porous material was the focus of this study, the reaction efficiency was ascertained by measuring the percentage weight of the porous material. As shown in Table 1, the amount of porous product increased with the temperature of the reaction. The highest product yield was possible at a reaction temperature of 800 °C.

2.2. Effect of Heating Time. The reaction progress varies with a change in heating time. The reaction progress is assessed by measuring the amount of porous material for different heating times in the range of 30–150 min. Since the amount of molten salt varies with heating time, it is important to predict the optimum reaction time for lowering the process cost and maximizing the product yield. The reaction temperature was set at 800 °C for studying the effect of heating time on the process efficiency. At the end of each experiment, the product was cooled down and weighed for estimation of weight loss. The experiments were performed in triplicates, and the mean values are shown in Table 2. The product weight reaches a constant value after 90 min of heating. For further testing, this reaction time was chosen as an optimum time condition.

Table 2. Effect of Reaction Time on Thermochemical Conversion of Waste Glass

| Time (min) | % weight before water treatment | % weight after water treatment | % yield |
|-----------|-------------------------------|-------------------------------|--------|
| 30        | 97.00                         | 88.90                         | 75.12  |
| 60        | 95.55                         | 88.86                         | 76.20  |
| 90        | 95.55                         | 87.5                          | 78.55  |
| 120       | 95.54                         | 87.0                          | 78.00  |
| 150       | 95.54                         | 86.9                          | 78.25  |

2.3. Effect of Relative Ratio of Reagents. The yield, porosity, and composition of the product also depend on the relative concentration of the waste glass, media, and flux. In this study, soda worked as a major reactant and precursor for a porous product, while salt provided a medium and acted like a solvent for glass. The mollusk shells in the reaction generated the calcareous material, organic matrix, and char. The calcareous material improved the fluidity of molten glass and reduced the melting point. The rock salt (sodium bicarbonate) reacted with the silicate backbone and broke the bonds to destroy the vitreous skeleton. It also formed carbon dioxide, which, on leaving the reaction, increased the porosity of the product. The amount of waste glass relative to one of the three reagents was varied, while the amounts of remaining reagents were kept constant. The findings of these experiments are summarized in Table 3. All reactions were carried out for 90 min at a fixed

Table 3. Optimization of the Combining Ratio of Materials

| glass:shell = variable | glass:soda = variable | glass:salt = variable |
|-----------------------|----------------------|----------------------|
| soda:salt = 20:20     | shell:salt = 20:20   | shell:soda = 20:20   |
| except no. 1, total weight = 100 g | except no. 1, total weight = 100 g | except no. 1, total weight = 100 g |
| % weight of product | % recovery after water treatment | % weight of product | % recovery after water treatment | % weight of product | % recovery after water treatment |
|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| 50:50                | 95.55                | 87.0                 | 81.22                | 63.01                | 84.65                | 74.0                 |
| 30:30                | 82.19                | 63.1                 | 82.56                | 63.02                | 82.69                | 63.7                 |
| 40:20                | 82.69                | 63.7                 | 82.69                | 63.7                 | 83.57                | 69.1                 |
| 50:10                | 84.47                | 74.7                 | 93.80                | 77.0                 | 94.16                | 72.03                |
| 60:00                | 94.81                | 78.43                | 95.69                | 85.6                 | 84.65                | 74.0                 |
temperature of 800 °C. The obtained product was washed to separate the water-soluble fractions from the product. The final product was given heat treatment at 400 °C to eliminate the traces of trapped vapor. When the weight ratio of glass to shells was the same, the product yield was maximum. The best scopic Analyses of the Porous Product.

644, 660, 677, 814, 874, 889, 991, 1612, 1624, 2357, 2978, 3018, 3057, 3093, 3111, 3122, 3134, 3147, 3181, 3250, 3265, 3462, 3676, 3745, and 3865 cm⁻¹. The possible functional groups and their vibrations are presented in Table 4. These peaks revealed

| peak   | intensity | groups | vibrations   |
|--------|-----------|--------|--------------|
| 413    | 37        | Ca−MoO | bending vibrations |
| 418    | 37        | Si−O−Si| bending vibrations |
| 455    | 69        | M−O−M | stretching vibrations |
| 521    | 88        | Si−O−Si| stretching vibrations |
| 595    | 99        | M−X   | stretching vibrations |
| 610    | 96        | M−X   | stretching vibrations |
| 636    | 96        | M−X   | stretching vibrations |
| 644    | 94        | M−X   | stretching vibrations |
| 660    | 94        | M−X   | stretching vibrations |
| 677    | 95        | M−X   | stretching vibrations |
| 814    | 94        | M−X   | stretching vibrations |
| 874    | 95        | C=Cl  | stretching vibrations |
| 889    | 96        | M=O   | stretching vibrations |
| 991    | 97        | M=O   | stretching vibrations |
| 1612   | 98        | C≡C   | stretching vibrations |
| 1624   | 99        | C≡C   | stretching vibrations |
| 2357   | 98        | CN    | stretching vibrations |
| 2978   | 97        | C=H   | stretching vibrations |
| 3018   | 99        | C=H   | stretching vibrations |
| 3030   | 98        | C=H   | stretching vibrations |
| 3057   | 98        | C=H   | stretching vibrations |
| 3093   | 98        | C=H   | stretching vibrations |
| 3111   | 98        | C=H   | stretching vibrations |
| 3122   | 97        | O−H, NH| stretching vibrations |
| 3134   | 97        | O−H, NH| stretching vibrations |
| 3147   | 96        | O−H, NH| stretching vibrations |
| 3181   | 96        | O−H, NH| stretching vibrations |
| 3250   | 96        | O−H, NH| stretching vibrations |
| 3265   | 93        | C≡N   | stretching vibrations |
| 3462   | 93        | C≡N   | stretching vibrations |
| 3676   | 92        | O−H   | stretching vibrations |
| 3745   | 92        | O−H   | stretching vibrations |
| 3865   | 92        | O−H   | stretching vibrations |

Table 4. Functional Groups and Possible Vibrations Obtained through FT-IR Analysis

The presence of silicates, carbon, metal oxides, and metal halides in the product. The carbon in the product is referred to the reaction of organic matter in mollusk shells with glass and other reactants. The peaks at 413, 418, and 455 cm⁻¹ reveal bending vibrations of Si−O−Si, while the peak at 521 cm⁻¹ shows the stretching vibration of O−Si−O. Another series of silicate-based

peaks was observed at 595, 610, 636, 644, 660, and 677 cm⁻¹. These peaks correspond to stretching vibrations of Si−O−Al and M−X. The peaks at 756 and 814 cm⁻¹ indicate C−Cl and C−H bonds, respectively. Similarly, some weak peaks at 874, 889, and 991 cm⁻¹ indicate stretching of glass-based metal oxides (M−O). The peaks at 1612, 1624, and 2357 cm⁻¹ are for the C−N stretching, C≡C stretching, and CNS functional groups. Peaks at 2978, 3018, 3057, 3093, 3111, 3122, 3134, 3147, 3181, 3250, 3265, 3462, 3676, 3745, and 3865 cm⁻¹ indicate OH. The presence of NH and NH₂ in the product can be attributed to proteinaceous compounds of mollusk shells, while OH originates from Si−OH or water trapped in the silicate backbone.

2.4. Fourier Transform Infrared (FT-IR) and Microscopic Analyses of the Porous Product. FT-IR analysis of porous glass revealed peaks at 413, 418, 455, 521, 595, 610, 636, 644, 660, 677, 814, 889, 991, 1612, 1624, 2357, 2978, 3018, 3057, 3093, 3111, 3122, 3134, 3147, 3181, 3250, 3265, 3462, 3676, 3745, and 3865 cm⁻¹. The possible functional groups and their vibrations are presented in Table 4. These peaks revealed
The concentration of the adsorbed direct blue dye under equilibrium can be determined as:

\[ q_e = \left( \frac{C_0 - C_e}{m_s} \right) \times V \]  

(1)

where \( C_0 \) is the initial concentration of the blue dye, \( C_e \) is the concentration of blue dye in solution under equilibrium, \( V \) is the volume of solution, and \( m_s \) is the weight of the adsorbent. The amount of adsorbent determines the number of active sites for dye adsorption. Therefore, an increase in adsorbent weight may increase the adsorption capacity. The adsorption capacity of the adsorbent was tested by varying the weight from 0.2 to 1.4 g. Figure 5b shows the trend of adsorption capacity with changing weight of the adsorbent. The adsorption curve revealed an increase in adsorption with weight. This increase can be attributed to the availability of more active sites for dye adsorption. The adsorption curve reached a steady state by increasing the adsorbent weight up to 1.2 g. The maximum adsorption was measured to be about 2.66 mg/g.

The adsorption ability of an adsorbent can also be measured from the adsorbent concentration. This effect was investigated by exposing the fixed amount of adsorbent to the various concentrations of the active blue dye. Figure 5c shows the trend of adsorption capacity over dye concentration in solution. It can be seen from the data plot that an increase in concentration of the dye promotes the adsorption of dye on the adsorbent. The trend may support the idea of multilayer adsorption due to the unique chemical and physical character of the adsorbent.

The adsorption capacity of porous glass was also tested by changing the pH of the solution. The phosphate buffer was used to control the pH of the solution. The adsorption capacity increased with an increase in pH but suddenly dropped to a minimum value at pH 7, as shown in Figure 5d.

### Table 5. Elemental Composition of the Porous Material Measured through EDX Analysis

| element | wt % | atom % |
|---------|------|--------|
| C K     | 7.60 | 12.58  |
| O K     | 53.93| 66.99  |
| Na K    | 0.92 | 0.80   |
| Al K    | 0.44 | 0.32   |
| Si K    | 5.21 | 3.68   |
| Ca K    | 30.36| 15.06  |
| Ti K    | 0.30 | 0.12   |
| Fe K    | 1.25 | 0.44   |
| total   | 100.00|        |

### Table 6. X-Ray Fluorescence Data of the Porous Material Obtained under Optimum Conditions

| SiO2 (wt %) | Al2O3 (wt %) | CaO (wt %) | Fe2O3 (wt %) | MgO (wt %) |
|-------------|--------------|------------|--------------|------------|
| 42.949      | 1.191        | 22.146     | 0.859        | 0.421      |
The acidic behavior of solution changed to neutral at a pH of 7. The high adsorption in acidic media was due to the charging of the adsorbent surface. The direct blue dye exists in the form of sodium salt of the sulfonic acid group. This salt changes to an acid at lower pH values by activating NH$_2$ groups, which interact with the protonated surface and Lewis acid moieties of the silicate backbone. These interactions promote the adsorption of the blue dye on the adsorbent surface. Similar results on the adsorption were observed when the adsorbent was exposed to solutions of varying pH, concentration, and adsorbent weight.
adsorption capacity of porous adsorbents were reported by El Nem et al. It was reported that adsorption of dye is primarily due to electrostatic interactions between the dye and protonated surface of the adsorbent.

2.6. Adsorption Isotherms of the Absorbent. The adsorption capacity of the porous material was also assessed by generating its adsorption isotherms. Different models are being used to explain the experimental results in the form of isothermic adsorption. In this work, the Langmuir and Freundlich adsorption models were used to explain the final concentration and adsorbed amount of the active blue dye. The Langmuir model explains the monolayer adsorption, whereas the Freundlich model is used to explain the heterogeneous adsorption process. The isotherms of adsorption suggested that the adsorption data fits both models due to the formation of micropores and mesopores during thermochemical conversion of glass into its porous form. Figure 6 shows Freundlich isotherms of the adsorbent for different adsorption times, weights, dye concentrations, and pH values. The mathematical form of the Freundlich adsorption model is

\[ q_e = K_F C_e^{1/n} \]  

(2)

In the linear form, this equation can be written as

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  

(3)

where \( q_e \) is the amount of dye adsorbed by a unit mass of adsorbent, \( C_e \) is the equilibrium concentration of the adsorbate, \( n \) is the Freundlich exponent, and \( K_F \) is the Freundlich constant. In regression analysis, the correlation coefficients of the Freundlich isotherm for the adsorbent dose, adsorption time, adsorbate concentration, and pH of solution were predicted to be about 0.975, 0.93, 0.98, and 0.978, respectively. These coefficient values were found to be higher than the coefficients of the Langmuir adsorption model. The coefficients of the Langmuir isotherms were estimated to be about 0.88, 0.746, 0.9, and 0.966, respectively. The slope of the data plots remained between −0.0296 and 0.735, which reveals the heterogeneous nature of the adsorbent. The adsorption of blue dye primarily occurred through the chemisorption mechanism. For an optimum concentration of the dye in the solution, \( 1/n \) was measured to be about −0.47, which also reflected the heterogeneity in the porous structure of the adsorbent. For optimum weight, pH, and time, \( 1/n \) increased from −0.47 to 0.747 by revealing the adsorption through a chemisorption process. Chemisorption played a dominant role in dye adsorption in the case of pH, particularly in low-pH solutions. The adsorbent surface gets charged during chemical adsorption and therefore reacts chemically with the dye. The adsorption data fit the Freundlich isotherm better than the Langmuir isotherm. The correlation coefficient of Freundlich isotherms varied from 0.93 to 0.98, which was slightly higher than the correlation coefficient of Langmuir isotherms.

Figure 7 shows the Langmuir isotherms of the adsorbent for different adsorption times, adsorbent weights, dye concentrations, and solution pH values. The mathematical form of the Langmuir adsorption model is

\[ \frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{b q_{\text{max}}} \times \frac{1}{C_e} \]  

(4)

where \( q_{\text{max}} \) and \( b \) are the Langmuir constants and \( \frac{1}{C_e} \) and \( \frac{1}{q_e} \) are the plot parameters for adsorption of dye onto the adsorbent surface. The effect of adsorbent amount, adsorbate concentration, and time on the Langmuir isotherms is reported in Figure 7. The regression constant of the Langmuir isotherms was found to be lower than that of the Freundlich isotherms. The high constant values of the Freundlich isotherms reveal that adsorption takes place in multilayers rather over a single layer due to the presence of silanol groups in the adsorbent. RL values of Langmuir isotherms suggested that the adsorption capacity depends on the adsorbent weight and pH of the solution but not on time and concentration. The data was fitted over widely used Langmuir and Freundlich models. A better correlation was observed between these models for individual isotherm plots. The adsorption data fit the Freundlich isotherm better than the Langmuir isotherm.

3. CONCLUSIONS

A glass-based porous material with high porosity and surface area was prepared through thermochemical conversion of waste glass in the presence of mollusk shells, soda, and rock salt. The maximum yield and porosity were achieved at a reaction temperature of 800 °C. The porous material was tested for its adsorption capacity by removing the blue dye from aqueous solutions and proposed as a remedy for the treatment of textile...
effluents. This adsorbent removed about 2.66 mg/g dye after 20 min of treatment time. The obtained data best fit the Freundlich adsorption model rather than the Langmuir adsorption model. In regression analysis, the correlation coefficients of the Freundlich model for adsorbent dose, contact time, concentration of adsorbate, and pH were measured to be about 0.975, 0.93, 0.98, and 0.978, respectively. These coefficients were found to be higher than those of the Langmuir model, which are 0.88, 0.746, 0.9, and 0.966, respectively. The slope range was between -0.296 and 0.735, which revealed the heterogeneous nature of the adsorbent. The dye adsorption mainly happened through the chemisorption process. The regression constant of Langmuir isotherms was found to be somewhat lower than that of the Freundlich isotherms. This indicates that adsorption occurred in multilayers rather over a single layer due to the presence of silanol groups in the product.

4. MATERIALS AND METHODS

The raw glass was empty water ampoules commonly used to prepare injections in hospitals and clinics. The empty ampoules were collected from waste bins of the District Head Quarter Hospital, Mardan, Pakistan. For this work, only colorless ampoules were chosen to avoid complications due to pigments contamination. The ampoules were made of soda glass. The ampoules were washed, cleaned, and placed in boiling water for 30 min. After the hot water treatment, ampoules were rinsed with distilled water and dried in an industrial oven. The dried ampoules were crushed into fine powder. A dry sieving method was used to obtain the powder of glass with an average particle size of 200 μm. The mollusk shells were collected from the sand of Badrai stream, which runs in the Swabi district of Khyber Pakhtunkhwa, Pakistan. The mollusk shells were dried, cleaned, and crushed into fine powder using a procedure similar to that used for ampoules. A dry sieving method was used to obtain the powder of mollusk shells with an average particle size of 200 μm.

4.1. Reactor Design. The waste glass was converted into its porous form through thermochemical processing in a cylindrical stainless steel reactor. The inner diameter of the cylinder was 6.7 cm, while its height was 13.97 cm. This custom-made reactor of cylindrical geometry had a lid for closure. The reactor cover had a 3.81 cm side drain to exhaust gases. The reactor was placed in a preheated top load furnace. A set of temperature sensors and thermocouples was used to monitor and control the furnace temperature. A nickel chrome resistance coil was used as heating filament to heat the material up to 1000 °C.

4.2. Formation of Nonvitreous Porous Glass. An intimate mixture of waste glass powder, mollusk shell powder, sodium bicarbonate, and sodium chloride was loaded into the reactor. The reactor was placed in a preheated furnace and heated up to the desired temperature. The ideal conditions for conversion of waste glass into porous product were explored by adjusting the reaction time, reaction temperature, and relative amount of reactants. The porous product was processed further to extract water-soluble fractions. The final product was crushed into powder with an average particle size of 200 μm.

The pore size, pore volume, and active surface area of the porous glass were analyzed using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. These tests were conducted using nitrogen gas as a standard adsorbate. The adsorption experiments were performed on a Quantachrome surface area analyzer. BJH surface area was measured to be about 11.344 m²/g, whereas BET surface area was about 28.017 m²/g. The size of the pores was calculated to be about 0.008 cc/g with an average pore radius of 1.459 nm.

4.3. Adsorption Study. The fine powder of the glass-based adsorbent was tested for adsorption of the direct blue dye. The adsorption capacity was measured for different concentrations of dye, pH values, adsorption times, and adsorbent doses. A solution of known dye concentration and pH was reacted with a fixed amount of adsorbent under continuous stirring. The adsorption experiments were conducted under ambient conditions. On completion of the adsorption test, the adsorbent was separated from the dye-containing solution through centrifugation. UV–visible spectroscopy was used to measure the concentration of dye in the solution before and after the adsorption experiment. The UV absorbance peak of the dye was obtained at 600 nm. As shown in Figure 8, the porous glass adsorbs protonated moieties from the solution of low pH by interacting with NH₂, OH, and N=N groups of the active blue dye. For higher pH values, the porous glass adsorbs the anionic form of dye.

Figure 8. Scheme of adsorption of the direct blue 15 dye on the protonated glass adsorbent.

The authors declare no competing financial interest.
ACKNOWLEDGMENTS

This work is sponsored by the King Saud University, Riyadh, Saudi Arabia, under the Research Group Project No. RG-1440-095.

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