Fixed-bed adsorption of the dye Chrysoidine R on ordered mesoporous carbon

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ABSTRACT

Herein, the efficiency of an ordered mesoporous carbon (OMC), synthesized through metal and halide free pathways, is evaluated to remove an anionic dye Chrysoidine R through fixed-bed adsorption. Potentially toxic azo dye, Chrysoidine R, was employed as a test and encouraging results are obtained. The bulk removal of the dye was accomplished with 99.77% column saturation and treatment of the exhausted bed of adsorbent with a suitable eluent resulted in almost 100% dye-recovery. The efficiency of the column remained almost unchanged in five adsorption/desorption cycles. The fixed-bed column studies clearly reveal that the OMC is a highly efficient and robust material for large-scale wastewater treatment applications.

Keywords: Fixed-bed adsorber; Ordered mesoporous carbon chrysoidine; Adsorption; Desorption

1. Introduction

The problem of water contamination is a long-standing issue worldwide. Despite being the most abundant natural resource, the water balance on the earth is largely affected and disturbed by the inefficient treatment of wastewater generated from various sources mainly, industrial, and agricultural sectors [1]. A large number of both organic and inorganic pollutants are released into the water bodies in the form of untreated agricultural and industrial effluents, the latter being the major source of water contamination [2]. The organic contaminants in industrial effluents [3] broadly include insecticides, pesticides [4], phenols [5], PCBs [6], dyestuffs [7], etc., whereas the inorganic pollutants chiefly comprise heavy metals [8], nutrients, and anions [9]. Coming on to the contamination of water bodies by dyes alone, per annum production of dyes all-round the globe is 800,000 tons, out of which, 64,000 tons are produced in India and 7,040 tons of untreated dye is emitted directly into the water-bodies [10]. The dyes discharged into the water not only contaminate it and disturb the aquatic ecosystem but also its aesthetic value is affected adversely. Textile industries are the key source of dye-pollution [11,12]. Azo dyes, containing –N=N– bonds, are majorly used synthetic organic dyes in textiles. Apart from their well-known toxicity, their reduction results in chemicals that are cancer-causing agents, and thus, they have the potential to drastically impair the environment and human health [13]. Out of all extensively employed techniques for water treatment [13–18], the supremacy of the adsorption technique in terms of operations, investment, effectivity, etc., is irrefutable [19,20]. The inertness of organic synthetic dyes, attributed to their structural complexity makes it difficult to treat them [10]. It is where the process of adsorption outplays the other water-remediation techniques. The major concern of researchers working in this area has been to

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develop adsorbents that are cost-effective and at the same time possess desirable attributes such as high surface area, large pore diameters, and pore volumes. To achieve maximal output from minimal input (adsorbent dosage), conventional dye-adsorbents such as activated carbon or other low-cost adsorbents, are replaced with mesoporous materials, especially, ordered mesoporous carbon (OMC). The inherent properties of the OMCs, such as exceptionally high surface area, large pore sizes, narrow pore size distribution, etc. [21–23], directly influence the reaction rates and adsorption capacities. OMCs have been employed to adsorb a wide range of small to huge and bulky molecules. The gases like N_2, CO_2, CH_4 [24], and heavy metal ions such as cadmium, chromium, arsenic, etc. [25], have been reportedly removed with the help of OMC. They have been found to be an efficient adsorbent for the removal of large and bulky organic moieties viz. dyes [26], antibiotics [27], alkaloids [28], etc.

The adsorbent in the present study was synthesized by soft-templating via a base-catalyzed two-phase separation technique [29] and batch adsorption and sequestration of the dye Chrysoidine R using the same adsorbent has also been successfully carried out by our research group [30].

Literature survey reveals that to examine the efficiency of the adsorbent, both batch as well as column operations, have been employed [31,32]. The practical utility of the method is however decided by the efficiency for bulk removal of dyes during column operations. In batch operations, the dye concentration decreases with time, whereas, during column operations, the adsorbent is always in contact with the same fresh adsorbate feed concentration. Thus, there occurs a disturbance in the concentration gradient at the adsorbate-adsorbent interface in the former case while in the latter case, the concentration gradient remains unaffected. Hence, the adsorption capacity of the adsorbent turns out to be higher in column operations [33–35]. The column studies are preferred to batch experiments when it comes to checking the commercial viability of the adsorbent. The usefulness of batch studies, on the other hand, is limited to fixing the process parameters for effective column operations [36].

The present paper discusses the fixed-bed column studies on the developed OMC for the bulk removal of Chrysoidine R, based on well-founded methods [37,38]. Chrysoidine R (Fig. 1) is a synthetic organic mono-azo dye used in textile industries. Its reduced form tends to generate toxic compounds by undergoing a series of chain reactions. It can be a causal-agent of carcinomas, liver-cell adenomas, and leukemia in animals on oral administration [39]. With an exhaustive literature survey, it has been ascertained
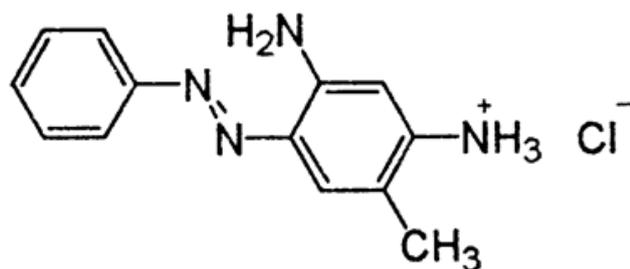
that so far, no study is available on the removal of any type of dye through a fixed fixed-bed adsorber of OMC. Another novelty of the present work is the use of a metal/halide-free variant of OMC as an adsorbent for the bulk removal of the dye Chrysoidine R.

2. Experimental

2.1. Synthesis of adsorbent

The OMC was synthesized via metal and halide-free soft-templating by employing the method originally proposed by Sakina and Baker [29]. The synthesis was carried out by phase separation technique, which was catalyzed by a base, ammonium hydroxide. In summary, in the first step of polymerization, ammonium hydroxide was added as a catalyst to a well-stirred reaction mixture of formaldehyde and resorcinol. The other step of condensation was initiated by adding a triblock copolymer, Poloxamer 407 (Pluronic F-127), and oxalic acid as structure-director and catalyst, respectively with constant stirring. The cloudy appearance of the mixture showed phase separation. At this point, the mixture was agitated for another 60 min and kept for 12 h when polymer gel was obtained. This gel underwent drying and curing at 353 K and then calcined at 673 K. The use of unconventional catalysts, ammonium hydroxide, and oxalic acid, instead of metal hydroxides and hydrochloric acid, respectively, eliminates the chance of product contamination with traces of metal and halide ions, which otherwise may devalue the product by blocking its surface active sites.

2.2. Characterization of the adsorbent

Three material characterization techniques, namely, gas physisorption experiments, small-angle X-ray diffraction (SAXRD), and transmission electron microscopy (TEM) were used to characterize the developed OMC. Cu Kα radiation in a PANalytical Empyrean instrument was employed to obtain SAXRD diffractograms of the material. Micromeritics TriStar II 3020 instrument (Unites States), operating at liquid nitrogen atmosphere, was used to record gas physisorption isotherms of samples degassed at 393 K under vacuum for a period of around 12 h. The physisorption data was used to derive the Barrett, Joyner, and Halenda pore-size distribution through the software provided with the instrument. The sample preparation for TEM was done by making a suspension of the material in acetone by ultrasonication and using tweezers, a 300 mesh, carbon-coated Cu grid was swiped through the prepared suspension. The grids dried overnight under a halogen lamp were then taken for examination under the electron microscope, JEOL 2011, supplied with a filament made of lanthanum hexaboride and a Gatan digital camera (operating voltage-200 kV).

2.3. Preliminary adsorption investigation

Dye, Chrysoidine R (A.R. grade) IUPAC name, 2,4-diamino-5-methylazobenzene; molecular formula, $C_{13}H_{15}ClN_4$; and molecular weight, 262.74 g/mol was purchased from M/s Merck, India. The chemical structure of Chrysoidine

Fig. 1. Structure of Chrysoidine R.

R is presented in Fig. 1. All other chemicals used were of AR grade. The effect of pH on the adsorption of Chrysoidine R was studied in batch experiments. The concentrations of dye solutions, before and after adsorption, were tracked spectrophotometrically using UV-vis spectrophotometer from M/s EI, India. The absorbance was recorded at a wavelength corresponding to maximum absorption for Chrysioidine R (λ_{max} = 449 nm).

To carry out batch experiments a known volume of dye solution (20 mL), of a known concentration (1×10^{-5} to 1×10^{-4} M) was taken into a conical flask of 100 mL capacity. The pH of the solution was adjusted (2–11) using 0.1 M NaOH and 0.1 M HCl solutions. The solution was then thoroughly shaken on a water-bath shaker until the equilibrium was attained. The solution was then centrifuged and the absorbance of supernatant was recorded spectrophotometrically at 449 nm. The equilibrium adsorption capacity was evaluated by the following formula:

$$q_e = \frac{(C_0 - C_e)V}{w} \tag{1}$$

where C_0 and C_e refer to the pre-adsorption and the equilibrium concentration of dye (mol/L), respectively, V is the volume of solution mixture (L), and w is the weight (g) of the adsorbent used.

2.4. Fixed-bed column studies

2.4.1. Fixed-bed column preparation

A glass column of known dimensions (height 30 cm and internal diameter 1 cm), fitted with glass wool as support, was used to prepare a fixed bed adsorber of the OMC material. A definite amount of the material, that is, 0.2 g was dispersed in 1,000 cm³ of double-distilled water and the slurry thus obtained was left to stand-overnight. A stream of double-distilled water was passed through the column, before feeding slurry to it. It prevented the chances of air-entrapment. The slurry was then carefully added to the glass column, which resulted in settling down of adsorbent particles by displacing the already-fed water and subsequent formation of a fixed-bed of column length 0.5 cm.

2.4.2. Methodology of bed exhaustion

The fixed-bed thus prepared was fed steadily with Chrysoidine R solution of known concentration. The dye solution of 1×10^{-3} M concentration, containing 107.7234 mg of Chrysoidine R at a pH of 7.0 was allowed to pass through it at a flow rate of 8 mL/min and aliquots of 10 mL dye solution were drawn. The concentration of each of the collected aliquots was determined with the help of UV-vis spectrophotometer. Initially, the dye concentrations of aliquot samples were almost negligible and slowly increased. It was observed that the concentration of successive aliquots was higher than that of the previous aliquot. The operation was stopped when the eluted dye concentration became equal to that of the initially fed solution and the fixed bed was now thought to be completely exhausted.

2.4.3. Recovery of dye and regeneration of exhausted bed

The completed exhausted column was then regenerated and the adsorbed dye was retrieved by passing a mixture of glacial acetic acid and water, in the ratio of 1:1 (v/v) through the column. The choice of eluent and the ratio of components were determined by a series of preliminary experiments. The flow of eluent was maintained at 8 mL/min and the collection of aliquots was continued until the aliquot concentration became zero. At zero aliquot concentration, all the dye was thought to be desorbed and the column was considered regenerated. The adsorption and desorption process thus carried out was considered as one cycle.

To test the reusability of the column and efficiency of the adsorbent as a fixed-bed adsorber, the dye of the same concentration was loaded again in the column and after achieving the exhaustion, desorption of the dye carried out in the similar manner to complete the next cycle. In the same manner, a total of five consecutive cycles were performed. It is also pertinent to note that all the adsorption–desorption fixed bed studies have been carried out at room temperature (30°C).

3. Results and discussion

3.1. Characterization of adsorbent

Despite being amorphous due to calcination at 400°C [40], the material still has an ordered mesopore structure that resulted in diffraction peaks in the SAXRD diffractogram (Fig. 2a). Clear reflections corresponding to Miller planes 100, 200, and 210 of mesopore structure that consisted of two-dimensional cylindrical pores, were observed. When viewed "end-on", the structure appears to be consisting of long pores (channels) that have a hexagonal arrangement. The peak positions were then used to evaluate the unit cell dimension as 13 nm.

The cylindrical nature of mesopores was further confirmed from nitrogen physisorption where type IV isotherm with H1 hysteresis was obtained and distinct capillary condensation was observed in 0.4–0.8 relative pressure range. The data retrieved from physisorption isotherm was also employed to study the pore size distribution and one sharp signal centered at 7.0 nm is indicative of narrow pore size distribution, that is, the structure consists of uniform pore sizes (Fig. 2b). The specific surface area was found to be 608 m²/g and the pore volume was equal to 0.63 cm³/g.

TEM images obtained at varying magnifications supported the findings of SAXRD and physisorption experiments. The long-range order and the existence of parallel, cylindrical pores can be confirmed from Fig. 3a, where the dark and bright regions show carbon matrix and pores, respectively. A more detailed structure is obtained at higher magnification (Fig. 3b) which shows individual parallel pores (side-on view). It should be noted that Fig. 3c presents the end-on view of mesopores. The inset picture of Fig. 3c is digital diffraction pattern (DDP) obtained by Fourier transform of the image. The DDP spots are identified and labeled with Miller indices of pore planes. In DDP, the arrangement and relative positions of spots confirm the presence of uniform, hexagonally arranged mesopores.
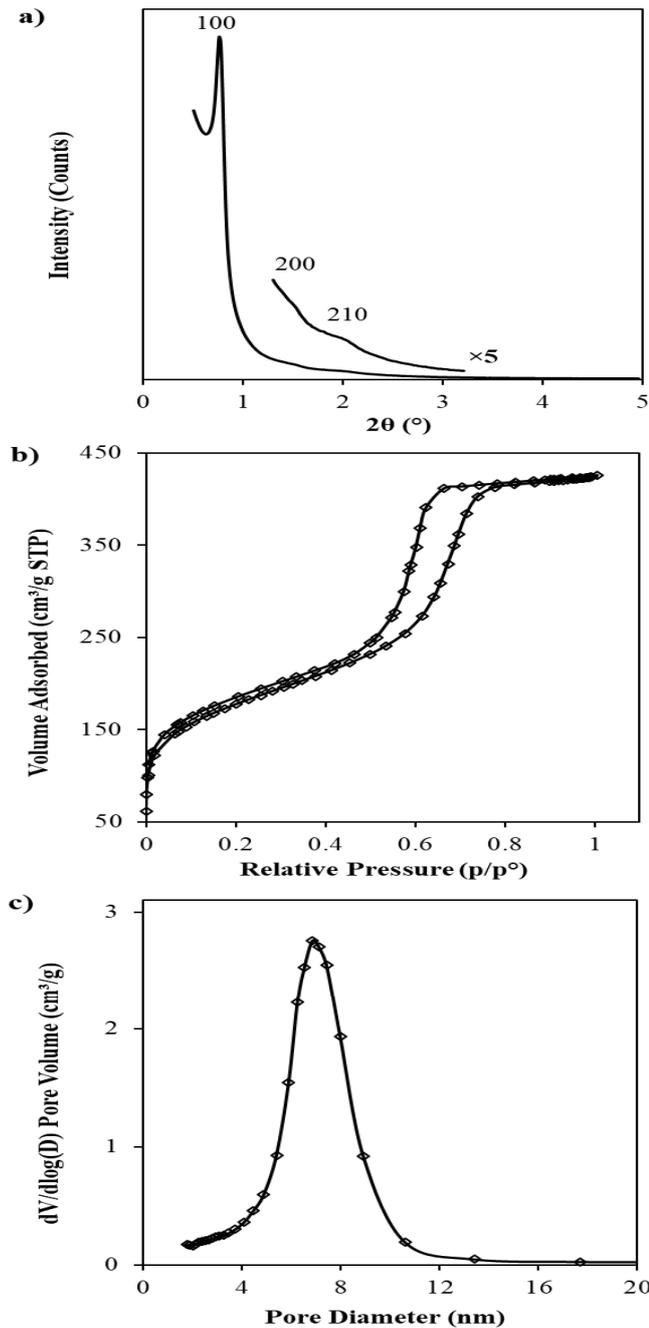
a)

b)

c)

Fig. 2. Physical characterization of the as-prepared OMC material: (a) small angle XRD pattern showing Miller indices of main planes and (b) nitrogen physisorption isotherm, and (c) pore size distribution derived from the physisorption data.

3.2. Influence of pH

The influence of pH on the removal of Chrysoidine R by OMC was monitored through batch experiments in the range of 2–11. It was found that dye removal continuously increases from pH 2.0 to 7.0 and then becomes almost constant (Table 1). The highest percentage removal was obtained at pH 7.0 and therefore this pH was selected to carry out all column operations.

3.3. Fixed-bed column studies

Owing to the limited applicability of batch processes, column studies are a tool to evaluate the utility of an adsorbent. Moreover, the column operations are faster, easier, and employed for bulk removal of the dye. A higher concentration gradient is maintained at the solid-solution interface as a constant dye concentration solution continuously remains in contact with the adsorbent. This results in higher exhaustivity and thus better efficiency of the material as an adsorbent than in the case of batch experiments [35].

The experiment was performed in the manner described in section 2.4 and a graph was plotted between the concentrations of the dye in eluted aliquots against the volume of collected samples and an S-shaped breakthrough curve was obtained (Fig. 4). The curve was then interpreted to evaluate the adsorption efficiency of the material in a fixed-bed based on percentage saturation. It can be observed in Fig. 4 that initially, up to 60 mL, no to negligible dye was detected in the eluted samples above which a continuous rise in dye concentration was recorded. The flattening in the curve was observed beyond 410 mL and at this point, the column was assumed to attain saturation. The nature of the curve indicates that the adsorption efficiency of the column was at a maximum initially, and then kept decreasing as the adsorption progressed till saturation point. It is also observed that the saturation of the adsorbent in the column started from the topmost zone and results in the formation of the primary adsorption zone (a region of evenly saturated column). This zone then passes down the length of the column and the concentration in the sample exiting the column becomes equal to the adsorbate feed concentration after a volume of 440 mL is collected. This marks the exhaustion of the column. The following equations were employed to analyze the breakthrough curve (Fig. 4) and also to evaluate the values of various parameters [35,41]:

$$t_x = \frac{V_x}{F_m} \tag{2}$$

$$t_\delta = \frac{V_x - V_b}{F_m} \tag{3}$$

$$\frac{\delta}{D} = \frac{t_\delta}{t_x - t_f} = \frac{t_\delta}{t_x + t_\delta(f-1)} = \frac{(V_x - V_b)}{V_b + f(V_x - V_b)} \tag{4}$$

$$f = 1 - \frac{t_f}{t_\delta} = \frac{M_s}{(V_x - V_b)C_0} \tag{5}$$

$$\text{Percentage saturation} = \frac{D + \delta(f-1)}{D} \times 100 \tag{6}$$

where δ represents primary adsorption zone length, t_x is the total time (minutes) taken for the establishment of primary adsorption zone, t_δ is the time (minutes) elapsed for the percolation of primary adsorption zone down its
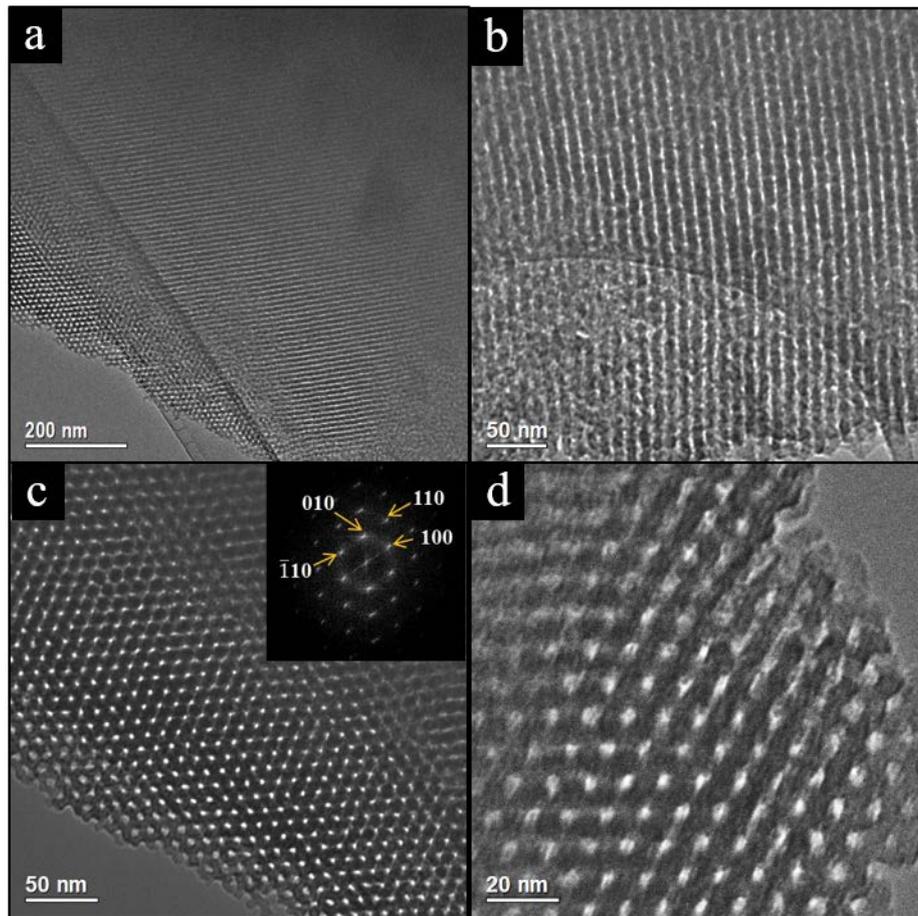
Fig. 3. TEM ordered mesoporous carbon: (a) long range order of pores, (b) cylindrical pores arranged in parallel, (c and d) hexagonally arranged mesopores viewed "end-on". The digital diffraction pattern (inset) as obtained from the image (c) indicating the Miller planes of pores.

Table 1
Effect of pH on the removal of Chrysoidine R over ordered mesoporous carbon (10 mg/20 mL) at 30°C

pH	% Dye removal
2.0	42.00
3.0	68.40
4.0	69.50
5.0	82.30
6.0	93.50
7.0	**98.00**
8.0	96.40
9.0	96.01
10.0	96.00
11.0	95.60

length, t_f is the time (minutes) taken for the initial formation of primary adsorption zone, V_x is the volume (mL) at C_x is the concentration at the point of column exhaustion), V_b is the volume at breakpoint, $F_{m'}$ D, and f represent the adsorbent's mass flow rate, bed-height and the column's fractional capacity at the breakthrough point, respectively.

The calculated values of column parameters are listed in Tables 2 and 3. Out of 107.7234 mg of Chrysoidine R that was fed to the 0.2 g of the adsorbent bed, more than 50% of the dye (56.05 mg) was adsorbed and 51.673 mg of the dye was collected as an eluate. It took 4,508.94 min (t_x) for the primary adsorption zone to establish and another 3,894.09 min (t_δ) to move down its length (δ). The calculated value shows that the primary adsorption zone took only 10 min to be formed. Through Eq. (5), values of various parameters were calculated and the percentage saturation of the column was evaluated as 99.77%, which validates the efficiency of the adsorbent column.

3.4. Reusability of column and dye retrieval

To test the reusability of the column, regeneration studies were done and the adsorbed dye was recovered using a mixture of glacial acetic acid and double-distilled water in the ratio 1:1 (v/v). This mixture was selected based on the high solubility of Chrysoidine R in acetic acid. The mixture was then run through the column and the concentration of every 25 mL aliquot collected was monitored spectrophotometrically. The operation continued until the solution exiting the column, had no dye detected
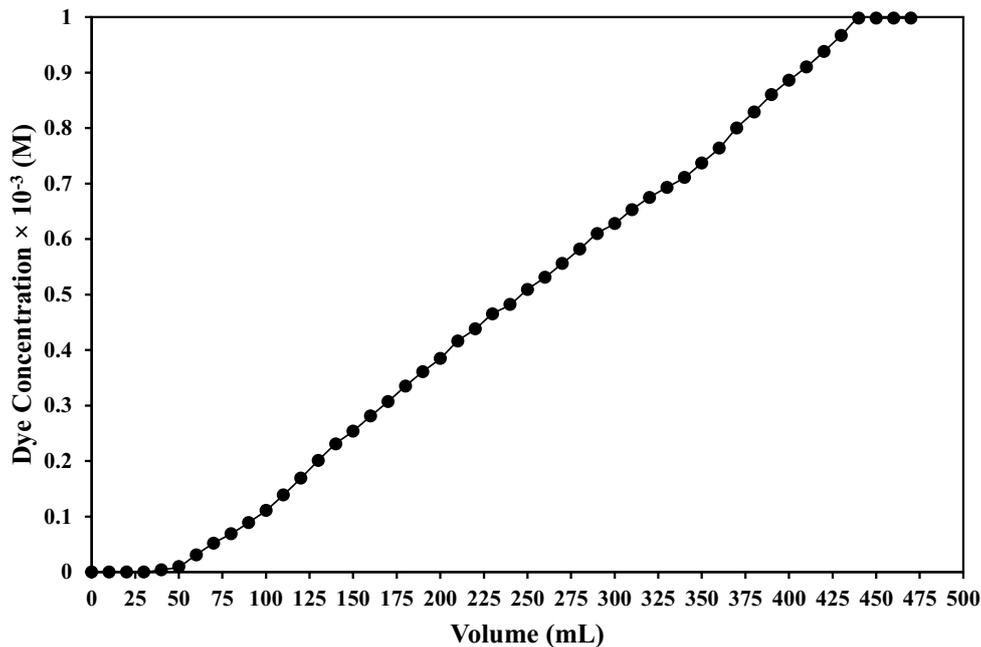
Fig. 4. Breakthrough curve for adsorption of Chrysoidine R over OMC in column operations (concentration of feed solution: 1×10^{-3} M, pH–7.0).

Table 2
Input data for calculations of Chrysoidine R-OMC fixed bed adsorber parameters

C_0 (M)	1×10^{-3}
C_x (M)	1×10^{-3}
C_b (M)	3.1×10^{-5}
V_x (mL)	440
V_b (mL)	60
$(V_x - V_b)$ (mL)	380
F_m (mg/cm²)	0.0975
D (cm)	0.5

Table 3
Values of parameters of Chrysoidine R-OMC fixed bed adsorber

t_x (min)	4,508.94
t_b (min)	3,894.09
t_f (min)	10
f	0.9974
δ (cm)	0.432
Percentage saturation	99.77

in it. The graph of volume of eluate vs. its concentration was plotted (Fig. 5) and it was found that after 26 aliquots of 25 mL eluent were drawn, the desorption percentage was 99.999% (51.672 mg of recovered dye) which marks almost 100% desorption. It can be seen in Fig. 5 that more than 90% of the dye was recovered with 250 mL of the eluent with dye recovery reaching 100% at 650 mL of the eluent. It shows that Chrysoidine R can be efficiently retrieved

from the adsorbent phase into the eluent provided its affinity towards the eluent is higher when compared to that for the adsorbent. The adsorption capacity of the column was found to be 258.37 mg/g in a neutral medium, which is quite a good value and gives us an insight into its prospects in the area of water treatment.

3.5. Column efficiency

The efficiency of the column was determined by performing five adsorption/desorption cycles. For the consecutive cycles, the column was loaded with the same dye concentration as in the first cycle, that is, 1×10^{-3} M and at pH 7.0, and the same procedure as discussed before it was repeated. The adsorbed dye was then eluted using the same eluent, a mixture of glacial acetic acid, and double-distilled water (1:1, v/v). To evaluate the efficiency of the column, percentage desorption in each of the cycles was determined. It can be observed in Fig. 6 that the percentage of dye recovery barely decreased from the second cycle – 99.992; third cycle – 99.890, fourth cycle 99.786 to fifth cycle 99.692 proving the fact that the efficacy of the adsorbent, the metal and halide free variant of OMC in the fixed-bed remained almost unaffected through the course of consecutive column operations.

4. Conclusion

The metal- and halide-free OMC was investigated for its potential to remove a mono-azo textile dye, Chrysoidine R, present in bulk. A fixed-bed of adsorbent was prepared and the results of column operations were analyzed. The column efficiency was evaluated in terms of column saturation percentage. The percentage of column
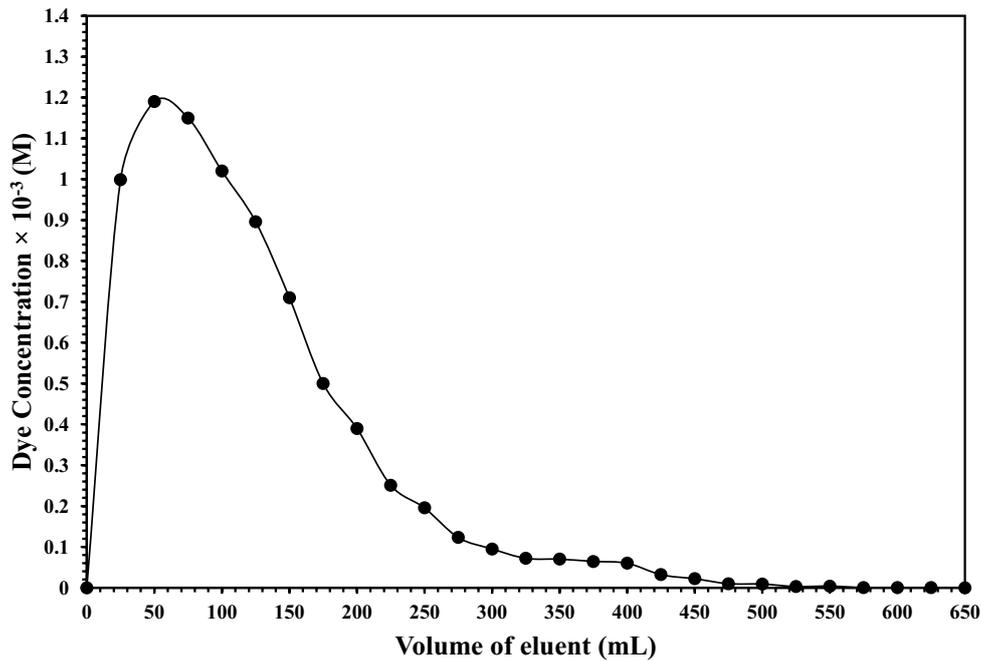
Fig. 5. Desorption of Chrysoidine R from exhausted column of OMC (eluent – glacial acetic acid: distilled water, 1:1, v/v).
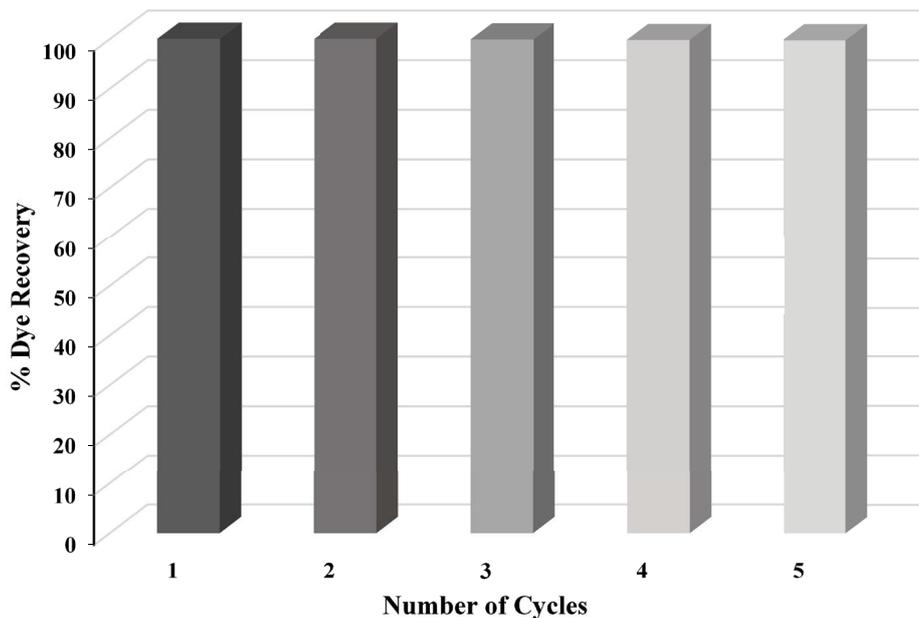

Fig. 6. Plot of percentage dye recovery vs. number of adsorption–desorption cycles.

saturation was found to be 99.77%. The exhausted column was regenerated by using a mixture of glacial acetic acid and double-distilled water. The regeneration of the column resulted in almost 100% dye retrieval. The column efficacy was further checked by performing five consecutive adsorption–desorption cycles. The percentage of dye recovery remained almost unaffected up to five cycles of adsorption–desorption. The percentage dye recovery for the first, second, third, fourth, and fifth cycles were found to be 99.999%, 99.992%, 99.890%, 99.786%, and 99.692%, respectively. Owing to the efficiency of the adsorbent material for the bulk removal of the dye without having adjusted the pH of the medium, that is, in a neutral medium, it can be safely concluded that dye-polluted water treatment with the adsorbent can be scaled-up.

Acknowledgments

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