



A Novel Self-Standing Porous Composite Bed of Kaolinite-Choline Chloride for Highly Efficient Removal of Anionic Azo Dye from Aqueous Solutions

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Abstract

Rapid industrial growth with uncontrolled effluent disposal has been taking its toll on the environment. One largely documented case of such uncontrolled waste disposal is from textile industries with significant amount of hazardous reactive dyes dissolved in the effluents. It is imperative that these dyes are taken care of before the effluent is discharged in the nearby water body. Thus, novel and cheap materials must be designed in order to enable efficient removal of these dye materials. Herein, we report the preparation of a high-performance porous novel composite bed of kaolinite and choline chloride. The self-standing porous composite bed enables easy application for separation of anionic dye through filtration. The composite bed constructed out of 1:1 w/w ratio of kaolinite and choline chloride is demonstrated to remove anionic azo dye, Remazol Red, from an aqueous system with high efficiency. The aqueous solution of the dye after treatment with the composite bed shows the same UV absorbance as the background equivalent absorbance. The electrostatic interaction between choline chloride and kaolinite in an alkaline environment results in strong physical attributes on the composite bed. We strongly believe that a highly capable composite material such as this will pave the way towards more competent, economical and non-destructive textile effluent treatment.

1. Introduction

Efficient removal of azo dyes from industrial effluents has been a long-standing technological challenge for the scientific community. Numerous researchers and their coworkers have employed several methods including physical, chemical, and biological approaches such as coagulation [1], membrane filtration [2], ion-exchange [3], adsorption [4-7], photo-degradation [8], enzymatic degradation [9] etc. for the effective treatment of these recalcitrant dyes. To date, fixed-bed column adsorption has been largely used for separating hazardous pollutants from wastewater via filtration [10]. Fixed-bed adsorption is advantageous over batch studies because of continuous treatment of substantial volume of wastewater [11]. On the contrary, batch equilibrium experiments are applicable only in laboratory scale for treating small quantity of wastewater [12]. The data obtained from fixed-bed

adsorption experiments can be used as a benchmark to scale up for industrial application [13]. Different types of substrates have been used in fixed-bed column for isolation of toxic pollutants from wastewater such as natural zeolites [10], chitosan-glutaraldehyde [12], activated carbon [14], *Eucalyptus sheathiana* bark [15], chitin [16], chitosan [17], eggshells [18], sawdust [19], pine cone [20], carbon-alumina composite [21] etc. However, major attention has been given on activated carbon due to high surface area, porous structure, and better adsorption performance [14]. However, the high cost for preparation and the difficulty in regeneration limits the industrial applications of activated carbon [9]. Therefore, focus has been shifted towards cost-effective alternate materials [15]. In this regard, naturally occurring clay minerals appear as attractive candidate for detoxification of industrial hazards. The low cost, high surface area, availability, potential for ion-exchange, lack of toxicity, a variety of surface and structural properties, molecular (organic) adsorption-desorption properties and chemical and mechanical stability make ground for the widespread application of clay minerals in fixed-bed column [2,22-24]. Srivastava et al. [25] reported the removal of nitrate from drinking water by bentonite using fixed-bed column. Baskan et al. [26] reported the efficient adsorption of arsenic in fixed-bed column using natural and modified clinoptilolite. The separation of copper in fixed-bed column from aqueous solution by chitosan-immobilized bentonite was studied by Futralan et al. [27]. However, the application of kaolinite based materials in fixed-bed column for separation of textile dyes has not been reported.

The free-flowing nature of powdered kaolinite restricts itself to be used in fixed-bed column for filtration purpose. Therefore, porous and channeled architecture should be made from kaolinite by appropriate modification with other materials. Here, choline chloride could be used as a suitable modifier, since it has already drawn attention from researchers for adsorption purpose. Wartelle et al. [28] reported the adsorption of chromate ion by choline chloride modified agricultural by-products. Karachalios et al. [29] studied the removal of nitrate from water via quaternized pine bark by utilizing an ionic liquid analogous to choline chloride. The quaternary structure of choline helps adsorb various ionic pollutants from wastewater. Therefore, modification with choline chloride could greatly alter the surface chemistry of kaolinite for adsorption purpose.

The objective of this study was to successfully fabricate a self-standing porous composite bed for the filtration of textile dyes from aqueous solution. Here, we report that the negatively charged functionalities of the fabricated filter bed perfectly restricted the penetration of a model azo dye (anionic) at alkaline pH. The effects of pH, dye concentration, time were thoroughly investigated for proper evaluation of the filtration performance. We highly expect that the fabricated filter bed will draw commercial interest for applications in removal of hazardous dyes from the effluents of textile, paint, pharmaceutical, food, printing, leather, cosmetic industries.

2. Experimental methods

2.1. Materials

Locally available kaolinite clay and choline chloride, supplied by Sigma-Aldrich, were utilized in this study for the fabrication of porous filter bed. Sodium hydroxide pellets and ethanol were purchased from Active Fine Chemicals Limited (Dhaka, Bangladesh). The dye removal performance of the fabricated bed was investigated with an aqueous solution of Remazol Red. This model dye was collected in an air-tight container from a nearby textile industry.

2.2. Fabrication of self-standing bed structure

0.95 g of kaolinite was suspended in 25 mL deionized water and stirred at room temperature (25 °C) for 4 hours. 2.5 mL of choline chloride with 0.38 g/mL density was gradually dropped into the

kaolinite suspension in order to maintain 1:1 ratio (w/w) of kaolinite to choline chloride solution. The resulting suspension was stirred in a magnetic stirrer for 4 hours. After 4 hours of stirring, the suspension was finely dispersed in a sonicator for 50 minutes. A syringe was cleaned properly with detergent, ethanol and deionized water and then dried. A small portion of cotton was put at the bottom of the syringe tube. The syringe was then filled with 20 mL co-solvent of 15% NaOH (w/w) and 95% ethanol (v/v) in 4:1 volume ratio. Kaolinite-choline chloride liquid suspension was added dropwise through a dropper. The composite bed was thus formed in the syringe. The cotton in the bottom of the syringe was then removed and the co solvent solution was also discharged from the bed. The composite bed in syringe was dried at 100 °C for 8 hours until the bed was completely dry. It is to be noted that care was taken when preparing the bed so that there was no gap between the sidewall of the syringe and the bed.

2.3. Material Characterization

FTIR 8400S spectrophotometer (Shimadzu Corporation, Japan) was used in this study to record the Fourier transform infrared (FTIR) spectra of the samples (wavenumber range: 4000-400 cm⁻¹; resolution: 4 cm⁻¹; number of scans: 30). Approximately 1 mg of samples was ground with 100 mg KBr by agate mortar and then pellets were made from the mixture by applying pressure. A thermogravimetric analyzer (TGA-50, Shimadzu, Japan) was used to record the thermal degradation profiles (thermograms) of the samples (Temperature range: 25 to 800 °C, nitrogen atmosphere, flow rate: 10 mL/minute, heating rate: 10 °C/minute, alumina cell, sample weight: 4 to 10 mg, total hold time at 800 °C: 5 minutes). The elemental composition of the samples was determined by taking the energy dispersive x-ray spectroscopy (EDS) spectra of the material (EDS with the FESEM model JEOL JSM 7600F). Finally, the filtration performance of the samples was investigated by a UV-VIS spectrophotometer UV-2100PC (Human Lab Instrument Co., Korea). A scanning electron microscope (JEOL JSM-6490LA, Tokyo, Japan) was used to investigate the morphological features of the samples (accelerating voltage: 20 kV ; electron mode: back-scattered). An X-ray diffractometer (Ultima IV, Rigaku Corporation, Japan) producing a Cu K α radiation of wavelength of 1.54 Å from a broad focus Cu tube (operated at 40 kV and 40 mA) was utilized to record the diffraction pattern. Scan rate was 3 °/minute within the theta range of 10° to 70°.

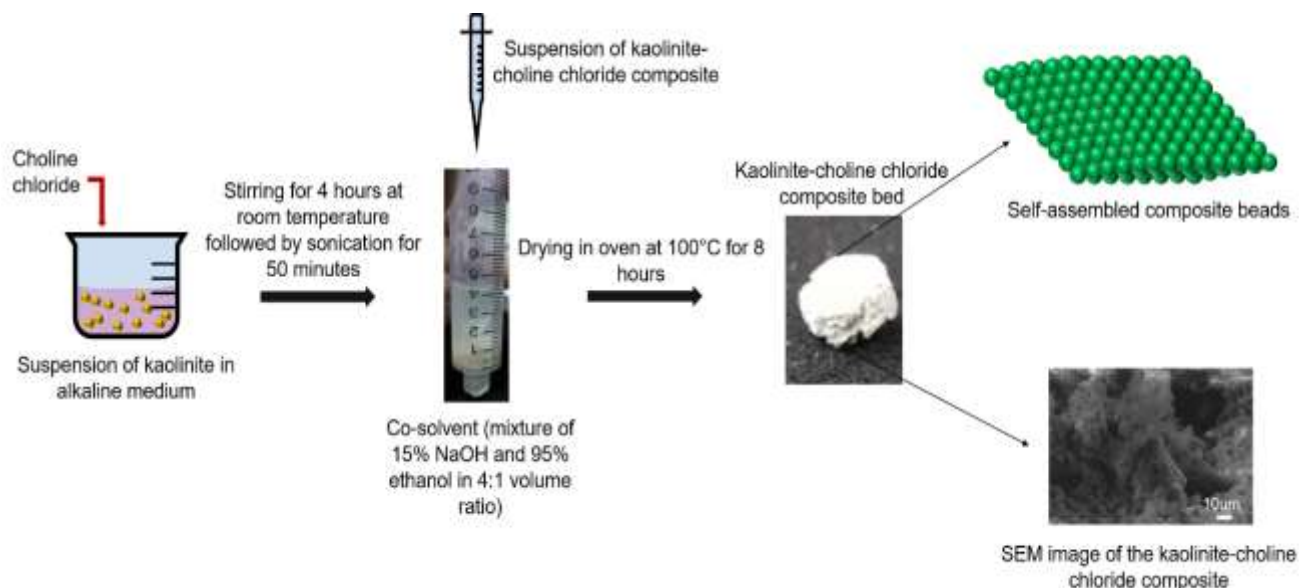
3. Results and Discussion

Chemically and thermally stable porous materials with interconnected channeled structures draw tremendous attention for potential applications in separation science due to their improved filtration efficiency. The dropwise and controlled addition of kaolinite/choline chloride mixture into a highly alkaline media in air resulted in the formation of composite beads (**Scheme 1**). The strong alkaline environment accelerated the breakdown of choline chloride and exposed the positive nitrogen terminal of the choline chloride. Performing the reaction in an aerated environment would also lead to the decomposition of the hydroxyl group of choline chloride (**Reaction 1**), as reported by Ramprasad et al. [30].



The ensuing electrostatic chemical interaction between positively charged N terminal of choline chloride and negatively charged kaolinite surface resulted in the fabrication of beads in the syringe. The newly formed composite beads settled to the bottom, where they came in contact with other beads resulting in self-assembled densely porous bed structures. In this fabrication process, the inner diameter of the syringe and cotton support at the bottom precisely controlled the shape of the fabricated filter bed.

Hereafter, the composite bed will be denoted as K-C composite bed. Kaolinite in itself is a free flowing powder and cannot be molded into a self-standing bed, while choline chloride can be synthesized in a strong film. The synthesized porous K-C composite bed showed the self-standing nature of the material, which appears to be a technological advantage from the application point of view.



Scheme 1. Fabrication process of kaolinite-choline chloride composite bed.

3.1. Characterization of porous composite bed

Figure 1a shows the FTIR spectra of kaolinite, choline chloride, and the K-C composite bed. The broad band in the green shaded region in the spectrum for choline chloride can be assigned for ν_{as} OH [31]. Interestingly, this peak was absent in the K-C composite bed. This provided evidence that the OH group of choline chloride ($[Me_3NCH_2CH_2OH]^+Cl^-$) had decomposed, most probably through the reaction route provided in **Reaction 1**. The band in the yellow shaded region at around 1478 cm^{-1} in the FTIR spectrum for choline chloride (**Figure 1a**) could be assigned for ρ CH₃ [31]. This particular vibration was still present in the K-C composite bed. Hence, this proved the presence of choline chloride in the K-C composite bed and the lack of peak in the green shaded region was not just because of the absence of choline chloride in the final material. It also indicated that the CH₃ bond of the choline chloride remained unchanged during the fabrication of the composite bed. We further analyzed the pristine K-C composite bed through thermogravimetric analysis (**Figure 1b**). We included the thermogravimetric curve of kaolinite as a reference in order to pinpoint the contribution of the constituents towards the mass loss of the K-C composite bed during thermal analysis. From **Figure 1b**, the weight loss up to 100°C can be attributed to the loss of adsorbed water which accounted for about 7.8% of the total mass. There was a sharp weight loss (47.7%) from about less than 200°C till 386°C . This weight loss was mainly due to the decomposition of the choline chloride from the K-C composite bed. The remaining mass was due to the inorganic kaolinite phase (44.5%). It must be mentioned here that we synthesized the K-C composite bed with 1:1 ratio of kaolinite and choline chloride. As the amount of choline chloride and kaolinite almost had the same weight ratio, thermogravimetric analysis provided evidence that the composite bed was synthesized with the intended ratio of kaolinite and choline chloride. A full elemental composition of the K-C composite bed, as determined through EDS, is provided in **Table 1**.

Table 1. Elemental composition of kaolinite-choline chloride composite bed.

Element	Mass (%)	Atom (%)
C	78.09	72.20
N	1.63	1.76
O	18.99	23.39
Na	0.3	0.53
Al	0.53	1.10
Si	0.45	0.97
Cl	0.02	0.06
Total	100.00	100.00

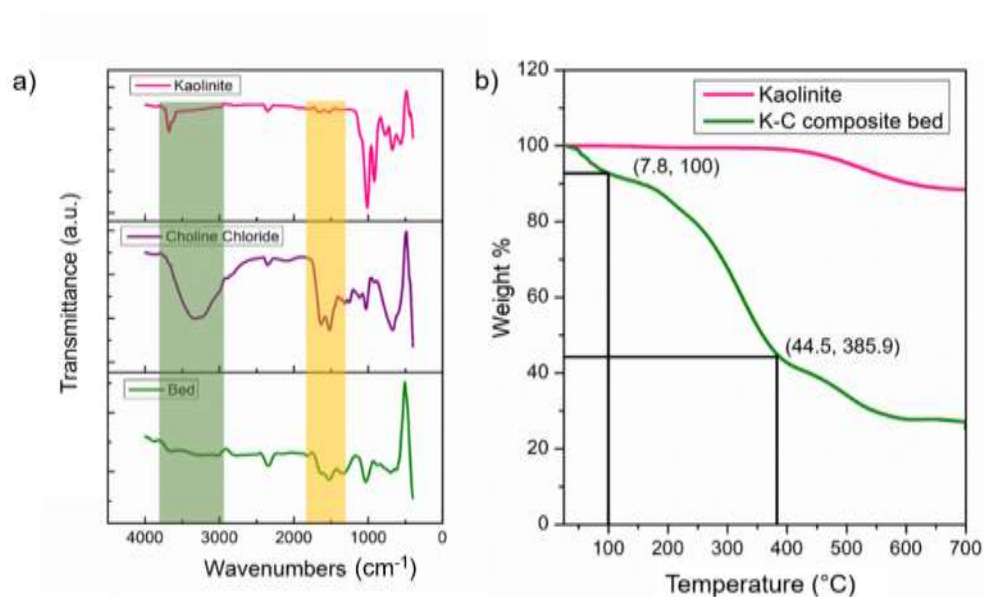


Figure 1: a) FTIR spectra of kaolinite, choline chloride and the K-C composite bed. The green shaded box and the yellow shaded box in the spectra highlight the regions where the difference in peaks of the three materials are observed. b) Thermogravimetric curve for kaolinite and the K-C composite bed.

Figure 2a shows the SEM micrographs of the pristine K-C composite bed. The porous nature of the composite bed is evident from the images with average particle size being bigger than 10 μ m. On the other hand, kaolinite itself has much smaller particle size with low porosity. The porous nature of the composite bed makes it an ideal candidate to be utilized as a medium for dye separation from aqueous solutions. XRD patterns of the K-C composite bed and kaolinite is reported in **Figure 2b**. The diffraction peaks at about 12° and 25° can be indexed to (001) and (002) crystal planes, respectively. The diffraction patterns of the composite bed closely resemble that of the kaolinite. However, a close inspection of the peaks of the two materials would reveal that there was a slight shift of the diffraction peaks towards the lower angle side for the composite material, meaning that the d spacing of the composite material is larger than the constituent kaolinite. This provided us evidence that rather than being a mere physical mixture of kaolinite and choline chloride, the constituents had a chemical interaction with each other in the final composite material. This slight shifting towards lower angle supports that choline chloride

could be partially intercalated inside the galleries of kaolinite thereby forming a highly stable composite bed structure. It has been widely reported in literature that intercalated composites display improved performance compared to the conventional composites [32].

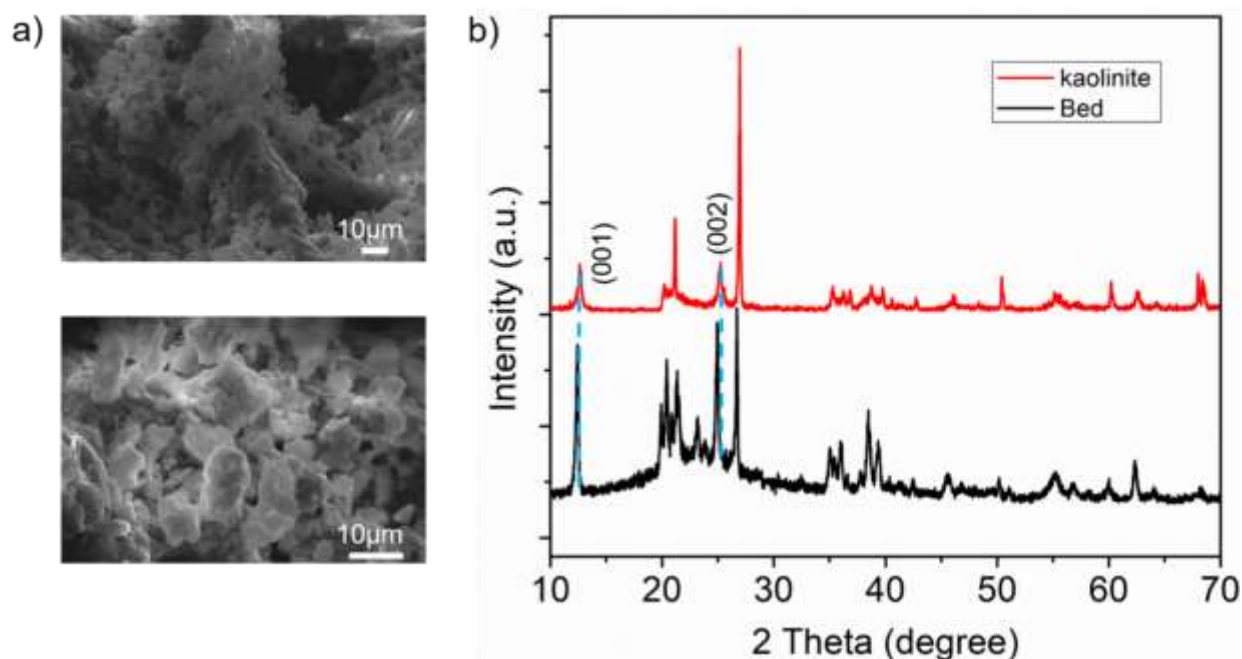


Figure 2. a) SEM micrographs of the K-C composite bed at different magnification. The porous nature of the bed is evident from the images. b) XRD pattern of kaolinite and the K-C composite bed. The dashed lines in the patterns indicate the relative positions of the peaks for the (001) and (002) crystal planes in kaolinite and the K-C composite bed.

3.2. Filter bed study

Due to the porous nature of the K-C composite bed with a negatively charged choline functionality ($\text{Me}_3\text{N}^+\text{CH}_2\text{CO}_2^-$), we hypothesized that the composite bed might facilitate to repulsive force for removal of anionic azo dyes from their aqueous solutions. This would provide an environmentally friendly solution of treating industrial effluent containing the hazardous azo dyes before it is discharged into the environment. In order to prove our hypothesis, we treated an aqueous solution of Remazol Red (RR), an anionic azo dye with the K-C composite bed. We treated a 50 mL 20 ppm aqueous solution of RR with the composite bed at a pH of 11.7. The justification of the chosen operating conditions is provided later. A setup similar to the one in [Figure 3a](#) was built in order to assess the efficiency of the K-C composite bed in removing RR from its aqueous solution. [Figure 3b](#) shows the UV/Vis spectra of the dye solution before treatment with the bed and also for every 5 mL solutions after treatment with the bed. As can be seen from the spectra, the aqueous solution of RR shows a peak at around 533 nm ([Figure 3b](#)). However, the solutions after treatment with the composite bed did not show any peak at all. This proves the efficient separation of RR from its aqueous solution. The absorbance of the treated solutions was equivalent to the background absorbance which signifies that almost all the RR dye was removed from the solution. The precise absorbance values at 533 nm wavelength for the treated solutions are around 0.05 a.u. which is resembled with the base value (0.047 a.u.) of fresh water. The absorbance of all the treated solutions was close to the absorbance of water, further justifying our statement. The highly efficient dye separation capability of the composite bed was exemplified by the accumulation of the removed RR on the surface of the composite bed. The efficient

removal of anionic azo dye from the solution means that the dye is almost completely deposited just by the surface of the composite bed and the bulk of the bed was no further needed to remove the dye from the solution. Thus, the efficiency of dye removal is independent of the bed thickness. This must be noted here that we further attempted to remove the dye from its solution using kaolinite only. However, kaolinite was not as efficient as the K-C composite bed to remove dye from the solution and the loosely packed powder nature of kaolinite means that the dye solution would just flow right through it. Meanwhile, the choline chloride film was too firm and non-porous for any solution to pass through it.

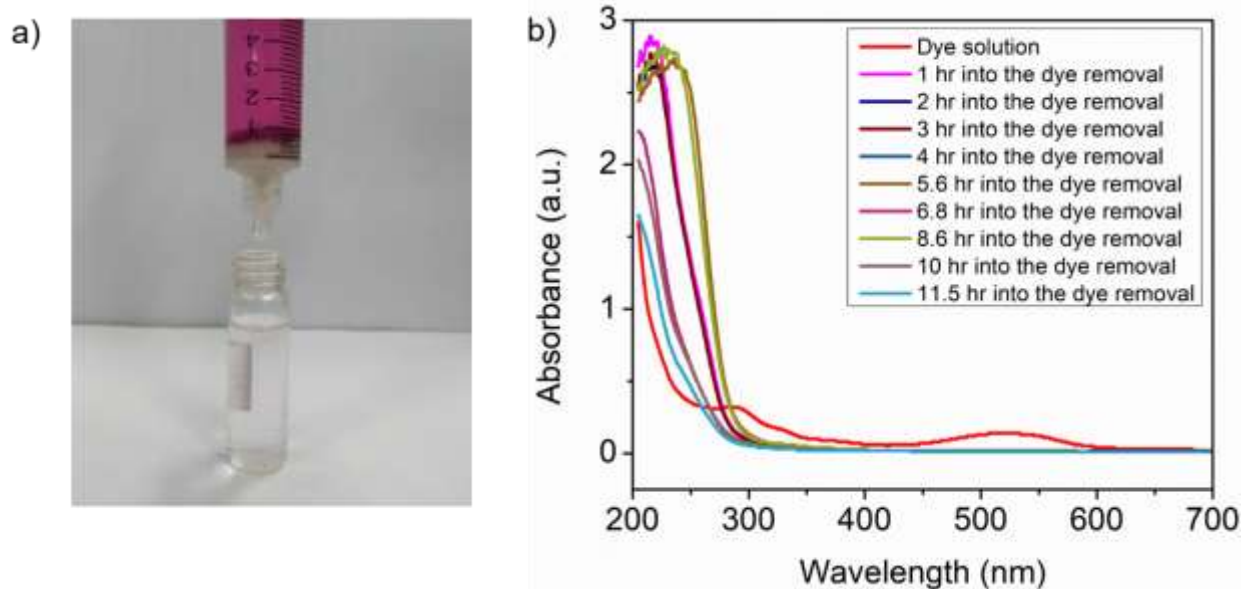


Figure 3. a) Photo of the setup for the aqueous Remazol Red treatment with the K-C composite bed. The thickness of the bed was 0.55 cm. b) UV/vis spectra of the treated solution at different time intervals. The time intervals represent the attainment of every 5 mL solution from the treatment with the K-C composite bed.

To find out the optimum condition for efficient dye separation from its aqueous solution, the effect of dye concentration and pH on the time required for the dye solution to filter through the bed was studied. The thickness of the bed was chosen to be 0.5 cm. **Figure 4a** shows the influence of RR concentration on time required for collecting every 5 mL of treated solution. The pH of all the solutions were kept constant at 11.7. As understood from **Figure 4a**, the time required for the dye removal increased as a function of increasing concentration. We suspect that at higher concentration, the accumulated dye on the surface of the composite bed would be blanketing the pores, making the passage of the solution progressively harder, hence requiring longer time. **Figure 4b** shows the influence of pH on the time required for collecting every 5 mL of the treated solution with the composite bed. The concentration of the RR solution was 20 ppm. The least time required among the two pH reported was at 11.7. At pH 9.1, the time required for collecting the solution increased significantly after a total collection of 15 mL solution and increased slowly thereafter. However, at pH 11.7, the time required for collecting every 5 mL solution was significantly lower than pH 9.1 and the time remained more or less the same throughout the dye removal operation. We did not perform the study beyond pH 11.7 because the highly alkaline solutions at a pH higher than 11.7 would pose an environmental threat in itself which would go against the overall goal of our research. Moreover, the bed was ineffective at pH 7 or lower as the physical integrity of the bed was severely compromised. We suspect that the physical cohesion of the bed at lower pH is the underlying reason behind the observed trend in time required for collecting the solutions. The bed was synthesized in an alkaline condition. Hence, at lower pH, the bed might have a tendency to disintegrate, most probably through a hydrolysis reaction. This translates into

having less porous structure at pH 9.1 and physical breakdown of beads at pH 7 to a film. Hence, pH values higher than 9.7 is best suited for efficient application of this composite. However, one does not need to go beyond pH 11.7 because at this pH, the dye removal was 100% and the speed of solution passing through the bed was also reasonably fast.

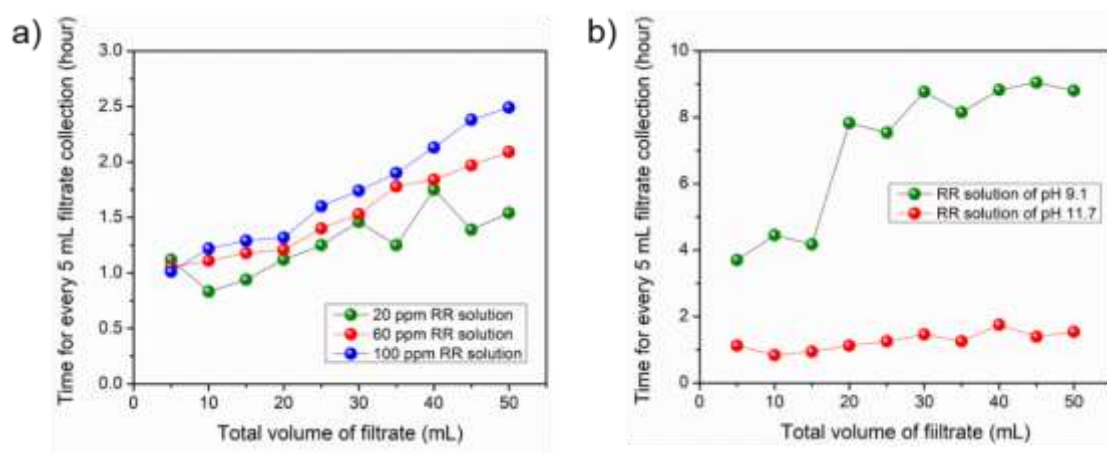


Figure 4. a) Effect of dye concentration on the time required for filtrate collection after treatment with the K-C composite bed, b) effect of pH on the time required for filtrate collection after treatment of the RR solution with the K-C composite bed. The thickness of the bed was chosen to be 0.55 cm.

An illustration for regeneration of filter bed, removal of dye and recycling of water is schematically presented in Figure 5. After filtration of dye solution, the bed was regenerated by atmospheric drying and removing the dried and solid dye layer from the bed surface. The colorless clean alkaline water was treated with dilute hydrochloric (HCl) acid to adjust pH at about 7. Recycling this water after distillation to the dyeing vat could reduce the consumption of fresh natural water. Besides, the dried dye would be possible to recycle for further dyeing of fabrics.

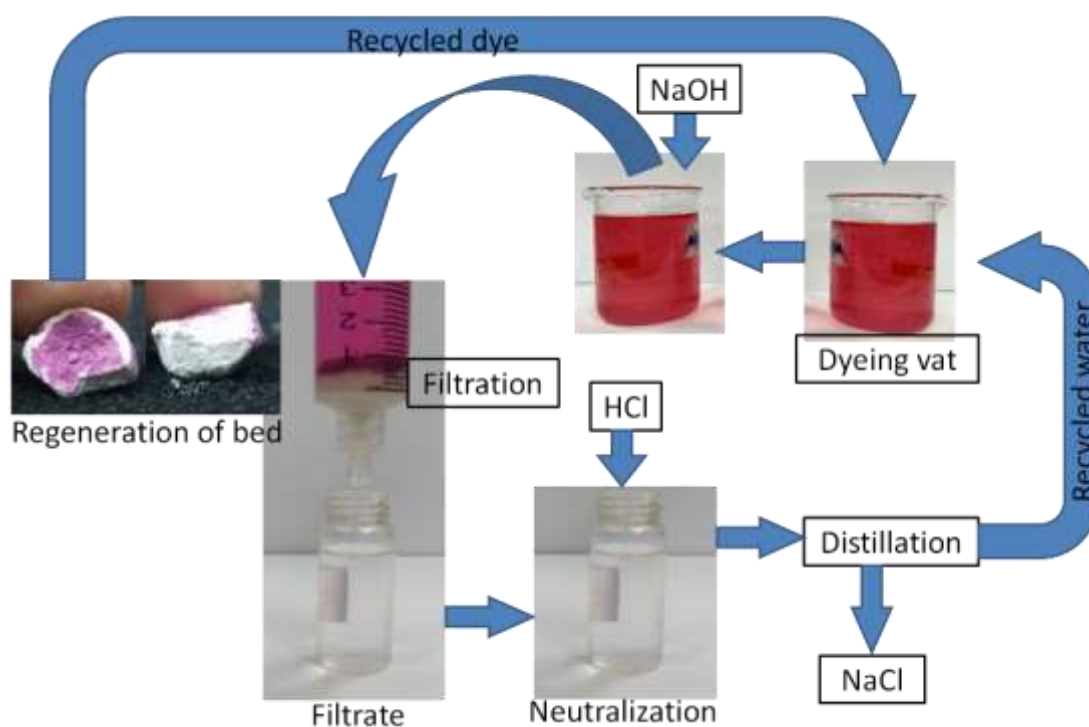


Figure 5. Schematic illustrations of regeneration of composites bed and recycling of water.

4. Conclusion

A self-standing and porous composite bed of kaolinite and choline chloride was synthesized with 1:1 w/w ratio of the constituents. Choline chloride and kaolinite had a chemical interaction with each other as determined through XRD and FTIR. The bed was highly efficient in removing RR dye from its aqueous solution. A 20 ppm aqueous solution at pH 11.7 was treated with the composite bed and the efficiency of dye removal was measured. It was found that the bed removed the dye from its solution with 100% efficiency. Due to the readiness of the dye removal at 20 ppm concentration by the composite bed, all the dye was removed by the surface of the bed and the bulk of the bed was not required to participate in the process. Hence, we found that the dye removal for this particular concentration was independent of bed thickness. Thus, we believe a competent bed for dye removal such as this would go a long way in answering the long lasting issues of water pollution due to textile industrial waste effluents. For future studies, the usability of porous composite bed of kaolinite and choline chloride for dyes removal from real industrial effluent will be tested and as comparison, a fixed bed column will be employed to investigate the effect of reactor design.

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Conflicts of interest

The authors declare no conflicts.

References

1. L.Tang, F. Xiao, Q. Wei, Y. Liu, Y. Zou, J. Liu, W. Sand, C. Chow, Removal of active dyes by ultrafiltration membrane pre-deposited with a PSFM coagulant: Performance and mechanism. *Chemosphere* 223 (2019)204–210. <https://doi.org/10.1016/j.chemosphere.2019.02.034>
2. W. Chen, J. Mo, X. Du, Z. Zhang, W. Zhang, Biomimetic dynamic membrane for aquatic dye removal. *Water Res.* 151 (2019) 243–251. <https://doi.org/10.1016/j.watres.2018.11.078>
3. M. Hisada, Y. Tomizawa, Y. Kawase, Removal kinetics of cationic azo-dye from aqueous solution by poly- γ -glutamic acid biosorbent: Contributions of adsorption and complexation/precipitation to Basic Orange 2 removal. *J. Environ. Chem. Eng.* 7 (2019) 103157. <https://doi.org/10.1016/j.jece.2019.103157>
4. M. M. Rahman. A. M. Zakaria, S.C. Dey, M. Ashaduzzaman, S. M. Shamsuddin, pH Controlled Reversible Interaction of Remazol Orange with Chitin. *Int. Lett. Chem. Phys. Astron.* 75 (2017) 25–36. <https://doi.org/10.18052/www.scipress.com/ilcpa.75.25>
5. S. Tighadouini, S. Radi, A New Silica Hybrid Material Based Adsorbent with NCC-Bipyrazolic Tripodal Receptor for Environmental Purpose. *Arab. J. Chem. Environ. Res.* 2 (2015) 76-99.
6. F. A. Ugbe, N. Abdus-Salam, Kinetics and thermodynamic modelling of natural and synthetic goethite for dyes scavenging from aqueous systems. *Arab. J. Chem. Environ. Res.* 7 (2020) 12-28.

7. A. D. N'diaye, Modeling of adsorption isotherms of dyes onto various adsorbents: A Short Review. *Arab. J. Chem. Environ. Res.* 5 (2018) 42-51.
8. A. K. M. M. Hasan, S. C. Dey, M. M. Rahman, A. M. Zakaria, M. Sarker, M. Ashaduzzaman, S. M. Shamsuddin, A kaolinite/TiO₂/ZnO-based novel ternary composite for photocatalytic degradation of anionic azo dyes. *Bull. Mater. Sci.* 43 (2020).
<https://doi.org/10.1007/s12034-019-1964-4>
9. A.N. Kagalkar, R. V. Khandare, S.P. Govindwar, Textile dye degradation potential of plant laccase significantly enhances upon augmentation with redox mediators. *RSC Adv.* 5 (2015) 80505–80517. <https://doi.org/10.1039/c5ra12454a>
10. L. Markovska, V. Meshko, V. Noveski, Adsorption of Basic Dyes in a Fixed Bed Column. *Korean J. Chem. Eng.* 18 (2001) 190–195. <https://doi.org/10.1007/BF02698458>
11. N. Gopal, M. Asaithambi, P. Sivakumar, V. Sivakumar, Continuous fixed bed adsorption studies of Rhodamine-B dye using polymer bound adsorbent, *Indian J. Chem. Technol.* 23 (2016) 53-58.
12. J. López-Cervantes, D. I. Sánchez-Machado, R.G. Sánchez-Duarte, M.A. Correa-Murrieta, Study of a fixed-bed column in the adsorption of an azo dye from an aqueous medium using a chitosan–glutaraldehyde biosorbent. *Adsorpt. Sci. Technol.* 36 (2018) 215–232. <https://doi.org/10.1177/0263617416688021>
13. S. Chakraborty, S. De, S. D.Gupta, J.K. Basu, Adsorption study for the removal of a basic dye: Experimental and modeling. *Chemosphere* 58 (2005) 1079–1086. <https://doi.org/10.1016/j.chemosphere.2004.09.066>
14. M. Nainamalai, M. Palani, B. Soundarajan, A.E. Allwin, Decolorization of synthetic dye wastewater using packed bed electro-adsorption column. *Chem. Eng. Process. - Process Intensif.* 130 (2018) 160–168. <https://doi.org/10.1016/j.cep.2018.06.013>
15. S. Afroze, T.K. Sen, H.M. Ang, Adsorption performance of continuous fixed bed column for the removal of methylene blue (MB) dye using Eucalyptus sheathiana bark biomass. *Res. Chem. Intermed.* 42 (2016) 2343–2364. <https://doi.org/10.1007/s11164-015-2153-8>
16. G. McKay, H.S. Blair, J.R. Gardner, The adsorption of dyes onto chitin in fixed bed columns and batch adsorbers. *J. Appl. Polym. Sci.* 29 (1984) 1499–1514. <https://doi.org/10.1002/app.1984.070290504>
17. V.M. Boddu, K. Abburi, J.L. Talbott, E.D. Smith, Removal of Hexavalent Chromium from Wastewater Using a New Composite Chitosan Biosorbent. *Environ. Sci. Technol.* 37 (2003) 4449–4456. <https://doi.org/10.1021/es021013a>
18. M. Chafi, S. Akazdam, C. Asrir, L. Sebbahi, B. Gourich, N. Barka, M. Essahli, Continuous Fixed Bed Reactor Application for Decolourization of Textile Effluent by Adsorption on NaOH Treated Eggshell. *Int. Scholarly Sci. Res. Innov.* 9 (2015) 1242-48. <https://doi.org/10.5281/ZENODO.1339009>
19. V.K. Garg, R. Gupta, A.B. Yadav, R. Kumar, Dye removal from aqueous solution by adsorption on treated sawdust. *Bioresour. Technol.* 89 (2003) 121–124. [https://doi.org/10.1016/S0960-8524\(03\)00058-0](https://doi.org/10.1016/S0960-8524(03)00058-0)
20. M.T. Yagub, T.K. Sen, S. Afroze, H.M. Ang, Fixed-bed dynamic column adsorption study of methylene blue (MB) onto pine cone. *Desalin. Water Treat.* 55 (2015) 1026–1039. <https://doi.org/10.1080/19443994.2014.924034>
21. P.A. Raut, M. Dutta, S. Sengupta, J. K. Basu, Alumina-carbon composite as an effective adsorbent for removal of Methylene Blue and Alizarin Red-s from aqueous solution, *Indian J.*

- Chem. Technol.* 20 (2013) 15-20.
22. A.A.Adeyemo, I.O.Adeoye, O.S.Bello, Adsorption of dyes using different types of clay: a review. *Appl. Water Sci.* 7 (2017) 543–568. <https://doi.org/10.1007/s13201-015-0322-y>
 23. A. Gürses, Ç. Doğar, M.Yalçın, M. Açikyildiz, R. Bayrak, S. Karaca, The adsorption kinetics of the cationic dye, methylene blue, onto clay. *J. Hazard. Mater.* 131 (2006) 217–228. <https://doi.org/10.1016/j.jhazmat.2005.09.036>
 24. H. H. Murray, Traditional and new applications for kaolin, smectite, and palygorskite: A general overview. *Appl. Clay Sci.* 17 (2000) 207–221. [https://doi.org/10.1016/S0169-1317\(00\)00016-8](https://doi.org/10.1016/S0169-1317(00)00016-8)
 25. A. Srivastava, S. P. Kumar, Adsorption of Nitrate from Ground Water using Indian Bentonite: Fixed Bed Column Study. *Int. J. Eng. Res. Technol.* 6 (2017) 390-94. <http://dx.doi.org/10.17577/IJERTV6IS050230>
 26. M.B. Baskan, A. Pala, Batch and fixed-bed column studies of arsenic adsorption on the natural and modified clinoptilolite. *Water. Air. Soil Pollut.* 225 (2014) 1798. <https://doi.org/10.1007/s11270-013-1798-4>
 27. C.M. Futralan, C.C.Kan, M.L.Dalida, C. Pascua, M.W.Wan, Fixed-bed column studies on the removal of copper using chitosan immobilized on bentonite. *Carbohydr. Polym.* 83 (2011) 697–704. <https://doi.org/10.1016/j.carbpol.2010.08.043>
 28. L.H. Wartelle, W.E. Marshall, Chromate ion adsorption by agricultural by-products modified with dimethyloldihydroxyethylene urea and choline chloride. *Water Res.* 39 (2005) 2869–2876. <https://doi.org/10.1016/j.watres.2005.05.001>
 29. A. Karachalios, M. Wazne, Nitrate removal from water by quaternized pine bark using choline based ionic liquid analogue. *J. Chem. Technol. Biotechnol.* 88 (2013) 664–671. <https://doi.org/10.1002/jctb.3883>
 30. D. Ramprasad, W.E. Carrloll, F.J. Waller, T. Mebrahtu, Betaine Synthesis via the Aqueous Oxidation of Choline Salts. *CHEMICAL INDUSTRIES-NEW YORK-MARCEL DEKKER-*, (2001) 361-370.
 31. C. Du, B. Zhao, X.B. Chen, N. Birbilis, H. Yang, Effect of water presence on choline chloride-2urea ionic liquid and coating platings from the hydrated ionic liquid. *Sci. Rep.* 6 (2016) 1-14. <https://doi.org/10.1038/srep29225>
 32. M. Bhattacharya, Polymer Nanocomposites—A Comparison between Carbon Nanotubes, Graphene, and Clay as Nanofillers. *Materials.* 9 (2016) 262. <https://doi.org/10.3390/ma9040262>

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