CHEMICAL ENGINEERING TRANSACTIONS
VOL. 86, 2021
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš

ISBN 978-88-95608-84-6; **ISSN** 2283-9216

Removal of Dyes from Wastewater using the Residue from the Chemical Recycling of Glass Cullet

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The unextracted residue, obtained after an extractive process from glass cullet with sodium hydroxide aqueous solution at 140°C for 2 hours, is mainly made of calcium and sodium silicate. It shows a high porosity and a large surface area. It could be active as an agent for the removal dyes from wastewater. In this paper Methyl Red (MR) was employed to evaluate the adsorbent properties of above residue. Aliquots of this residue were maintained at room temperature under constant stirring with 0.025-0.5 g/L of MR aqueous solution by using a liquid/solid ratio from 50 to 500 mL/g and up to 24 hours. The results have shown an effective removal of MR within one hour for MR concentration of 0.5 g/L and within 30 minutes and for MR concentration ≤ 0.25 g/L with liquid/solid ratio < 100 mL/g. The performance of the residue as an adsorbent contributes to increase the environmental sustainability of glass recycling treatment and further decreases the amount of waste to be delivered to landfill.

1. Introduction

The use of dyes in many industries (i.e. textiles, paper, tanning, food, pharmaceuticals, cosmetics, etc.) causes serious environmental problems. A large amount of these dyes is discharged into watercourses and rivers. They are considered among the most dangerous contaminants in aquatic environments and therefore removing the dye from water and wastewater is necessary (Aseel et al., 2017). Most dyes are characterized by an aromatic structure; thus, they are very stable to light and oxidizing treatments. Since they are also resistant to the biodegradation, their absorption on activated carbon is considered a suitable alternative to these treatments (Song et al., 2012). Nevertheless, even if activated carbon (AC) remains a popular adsorbent, having numerous potentials for dyes' removal from wastewater, its purchasing cost commercially limits the use (Ahmad et al., 2019). In recent years, many studies have been published in the literature that proposed the use of natural substances (lemon grass, rice husk, watermelon, etc.) to obtain adsorbents capturing various dyes from wastewater (Ahmad et al., 2019; Mahmoud et al., 2018; Namasivayam et al., 2002). These can replace current available activated carbon and thus reduce costs. This work studies the performance of the residue, obtained from the chemical recycling of glass, for the adsorption of dyes from wastewater. Among the dyes, commonly used to test the adsorption properties of materials, there are the azo-compounds that are characterized by the presence of one or more double bonds – N = N – (Methyl Red, Methyl Orange and Aniline Yellow) (Ghorbani et al., 2019; Roik et al., 2021; Zaheer et al., 2019). In this paper, the Methyl Red (MR) has been tested. It is a mono-azo dye, which is classified as a toxic, mutagenic or carcinogenic pollutant. Its discharges into the receiving watercourses has negative effects for both aquatic ecosystems and human health. It causes eyes and skins sensitization, pharyngeal, irritations to digestive tract when swallowed and/or inhaled (Ahmad et al., 2019). A previous research has shown that the treatment of glass with aqueous solutions of NaOH extracts a quantity of silica equal to the 40 % at 105°C and over 50 % by operating at higher temperatures (Mavilia et al., 2000; Mavilia et al., 2001). Together with the aqueous extract of sodium silicate, that represents the main product, a residue mainly made of calcium and sodium silicate was obtained. This residue represents the unextracted part

of glass and it is equal to 45-50 (% wt.) of the original glass sample (Catalfamo et al., 2004). The study of its properties has shown a significant increase in the surface area and porosity. The use of glass residue could be an alternative to landfilling (Abukhadra et al., 2019; Hussain et al., 2019), hence, this approach is an important contribution to the eco-sustainability of glass recycling.
The aim of this work is the study of the performance of the unextracted glass residue as an adsorbent of dyes in the treatment of industrial wastewater.

2. Materials and methods

2.1 Samples

Experimental tests were carried out in duplicate on samples of post-use amber glass bottles (GPU), after crushing, grinding and sieving up to less than 150 µm diameter of particles. Two aliquots of each sample were dried at 110 °C for 2 hours and mixed with 5 M NaOH aqueous solution in a liquid/solid ratio = 3 mL/g. The extraction, in a closed reactor, was carried out under constant stirring at 140 °C for 2 hours. At the end, the remaining solid phase, named unextracted residue (UR), was filtered, washed with deionized water and then dried at 110 °C for 2 hours. The UR was then analyzed as given in Section 2.4.

2.2 Preparation of Methyl Red aqueous solution

Methyl Red (molecular weight is 269.3 g/mol) was used as dye for the adsorption tests. It was supplied by Sigma-Aldrich. A stock solution of 0.5 g/L of MR was prepared by dissolving 0.5 g of MR in 1 L of deionized water. Solutions of different initial concentration were prepared by serial dilution process from the initial stock solution.

2.3 Adsorption studies

To study the adsorption properties, aliquots of each sample of UR from 0.1 to 1.0 g were mixed in an Erlenmeyer flask with MR aqueous solution from 10 to 50 mL, resulting in a concentration ranging from 0.025 to 1 g/L with pH strongly basic (pH > 11). HCl was added for adjusting the pH at desired values (2 and 9). The samples were constantly stirred and kept at room temperature up to 24 hours. At pre-established intervals, aliquots of slurry were collected, filtered with a 0.45-micron Millipore filter and analyzed for determine the MR.
To determine the uptake capacity of dye, from the aqueous solutions, by the adsorbent at the equilibrium (q_e) and the uptake capacity at the time t (q_t), the following equations were used (Ozbay et al., 2015):

$$q_e = \left(C_o - C_e\right) \cdot V / S \tag{1}$$

$$q_t = \left(C_o - C_t\right) \cdot V / S \tag{2}$$

where q_e is the amount of dye fixed per unit of adsorbent mass at equilibrium (mg/g); q_t is the amount of dye fixed per unit of adsorbent mass (mg/g) at any time t; C_o, C_e and C_t are respectively the concentrations of the dye in the liquid phase (g/L) at the beginning, equilibrium and any time t; V is the volume of the dye solution (L); and S is the amount of adsorbent used (g).
The percentage of the dye removal, q_r (%), is given by:

$$q_r = \left(C_o - C_e\right) / C_o \cdot 100 \tag{3}$$

The concentration of MR in the filtrates after and before adsorption was determined by using a UV/VIS/NIR spectrophotometer (Perkin Elmer Lambda 750) by setting the wavelength at 513 nm. The calibration curve method was used to determine the concentration of MR.

2.4 Characterization

Composition, shape, structure and surface area were respectively determined by X-Ray Fluorescence (XRF), Scanning Electron Microscopy (SEM) and Nitrogen Physical Adsorption (BET) analyses. The composition was carried out using a RIGAKU SUPREMINI 200. The morphological analysis of the surface features was carried out using a focused ion dual beam/scanning electron microscope (FIB-SEM ZEISS Crossbeam 54, ZEISS, Obwerkochen, Germany). The determination of surface area and average diameter were carried out using Micromeritics ASAP2010 volumetric adsorption analyzer. The surface area was measured using Brunauer-Emmett-Teller (BET).

3. Results and discussions

3.1 Extraction, surface morphologies, surface area and pore characteristics

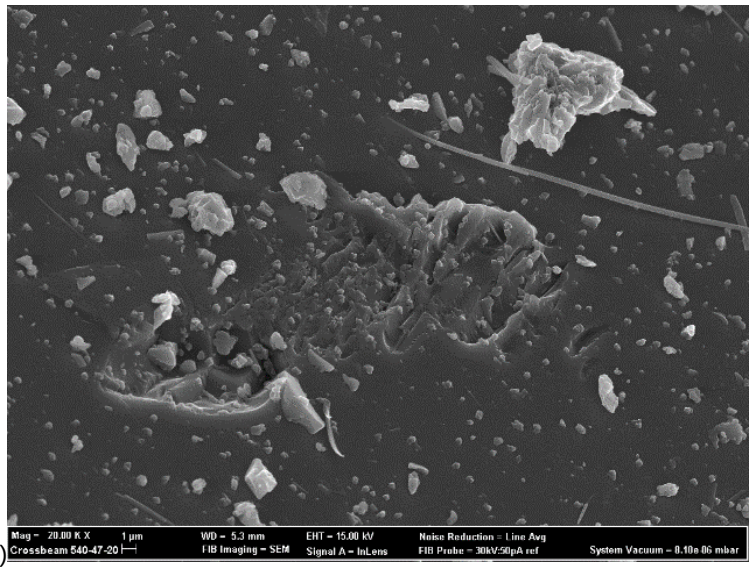
Table 1 reports the chemical composition of GPU and UR with respect to the main constituents. Decreases in the contents of SiO_2 and Na_2O and increases of CaO in the UR were found compared to the GPU. The treatment of the post-use glass powder with aqueous solutions of sodium alkali extracts the 51% (in weight) of silica, respect to the initial sample. UR amounts to 50%, compared to the virgin glass, and mainly contains the silica, as calcium and/or sodium silicate, insoluble in the conditions of this treatment.

Table 1: Percentages (wt %) of main constituents of post-use glass (GPU) and unextracted residue (UR).

	SiO_2	Na_2O	CaO	MgO	Al_2O_3	Others
GPU	70.6	12.1	12.5	2.4	2.1	3.1
UR	40.1	20.1	27.	4.2	3.8	4.3

SEM images of the glass, before (Figure 1a) and after (Figure 1b) the treatment, show that the original glass particles have been attacked and transformed from a compact form into a porous one.

(a)



(b)

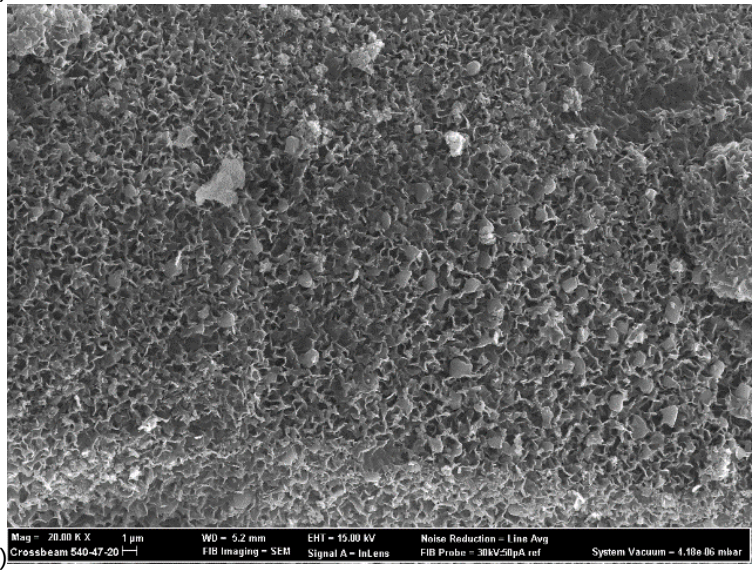


Figure 1: SEM images of the (a) post-use glass (GPU) and (b) unextracted residue (UR).

The BET analysis confirmed the increase of surface area and porosity (Table 2). The treatment with NaOH promoted the mesoporous formations that resulted in UR higher surface area in comparison to GPU.

Table 2: Surface area and average diameter of post-use glass (GPU) and unextracted residue (UR).

	GPU	UR
Surface area BET (m^2/g)	5,5	96,4
Diameter (Å)	17,83	117,7

3.2 Effect of pH

Tests conducted by contacting UR and 0.5 g/L of MR solution for 24 hours showed no adsorption at pH > 9. By decreasing the pH, removed amounts of less than 30% were observed. Figure 2 reports the effects of pH on MR removal. At pH 9, low rates of MR removal (less than 30%) were obtained. Tests conducted at pH 2 showed that the MR removal was up to 98.8%.
The electrostatic repulsion between the deprotonated form of the MR and the silica matrix, at pH ≥ 9, may be the reason for this evidence. The addition of acid, to vary the pH until 2, leads to the reconstitution of the acid form of MR and promotes the association via hydrogen bonds between the silicate and the MR.

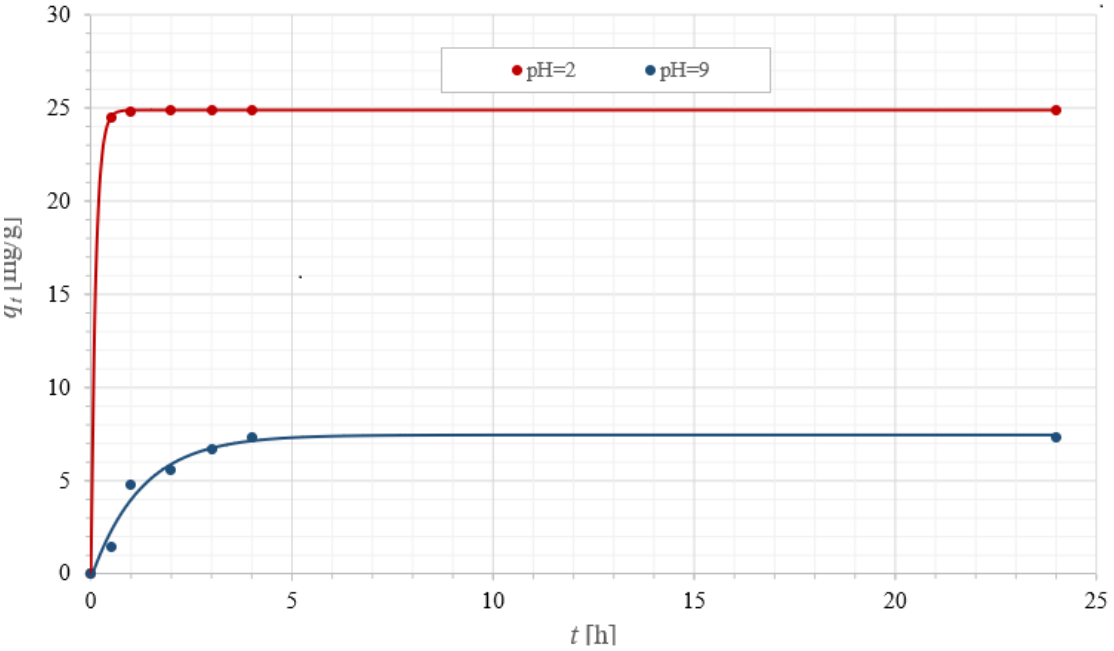


Figure 2: Effect of pH on the removal of 0.5 g/L MR (Methyl Red) aqueous solution after 24 hours of contact with 1 g of UR (Unextracted Residue, V = 50 mL)

3.3 Effect of initial dye concentration on the adsorption equilibrium

By setting the contact time to 24 hours, the effect of the MR concentration on the removal efficiency was evaluated in the range from 0.025 to 0.5 g/L. The results are shown in Table 3. A total removal of the dye was observed with concentrations < 0.5 g/L, as well as a variation of color of the solution that changes from pink to colorless. An adsorption of 98.8 % was obtained with concentration equal to 0.5 g/L, whereas with higher concentrations (data non reported), it reached the value of 80 %. Presumably, with higher initial concentrations of dye, the number of molecules competing for the sites available on the UR surface is high, with a consequent slight decrease in the adsorption capacity.

Table 3: Amount of MR (Methyl Red) removed from UR (Unextracted Residue) as a function of the initial concentration of dye (UR = 1 g, V= 50 mL).

Initial MR		Adsorbed MR	
g/L	mg	mg	%*
0.025	1.25	1.25	100
0.250	12.50	12.50	100
0.500	25.00	24.70	98.8

*(Adsorbed MR mg x 100)/ Initial MR mg

3.4 Effect of contact time and the adsorption equilibrium

Table 4 shows the effects of contact time on removal of MR from aqueous solutions. Batch adsorption tests showed that equilibrium conditions were reached within 30 minutes for MR concentration equal to 0.25 g/L, within one hour for MR concentration of 0.5 g/L with a liquid/solid ratio of 50 mL/g. The rapid adsorption was presumably due to the availability of many surface sites for the process.
By setting the contact time to one hour, the effect of the liquid/solid ratio was valued in the range from 50 to 500 mL/g on the removal of MR from concentration solution < 0.5 g/L. The results showed that for L/S ratio until 100 mL/g, the total removal of MR from solution < 0.25 g/L was obtained within 30 minutes, whereas one hour was required for 0.5 g/L MR solution. L/S > 100 mL/g (up to 500 mL/g), high percentages of removal, amounting to 98%, were still observed.

Table 4: Quantity of MR (Methyl Red) adsorbed by 1g of UR (Unextracted Residue) in the time range 0.5-24 h (V = 50 mL, MR = 0.25 and 0.5 g/L)

MR	MR adsorbed (mg) and removed (%) after									
	0.25 h		0.5 h		1.0 h		5.0 h		24 h	
g/L	mg	%	mg	%	mg	%	mg	%	mg	%
0.25	12.3	98.4	12.5	100	12.5	100	12.5	100	12.5	100
0.50	24.4	97.6	24.5	98.0	24.8	99.2	24.9	99.5	24.8	99.2

4. Conclusions

The treatment of post-use glass with 5 M NaOH aqueous solution for 2 hours at 140°C extracts over 50 % of silica. In these experimental conditions, the insoluble sodium and/or calcium silicates remain in the solid residue unextracted and amount to ca. the 50%. This unextracted residue presents a specific surface area that is approximately twenty times greater than that of untreated glass. The residue has also shown an effective removal of methyl red within one hour for dye concentrations of 0.5 g/L and within 30 minutes for concentrations < 0.25 g/L for a liquid/solid ratio < 100 mL/g. 1 g di unextracted residue adsorbs up to 245 mg/g in 1 hour from 0.5 g/L MR aqueous solutions.
The residue performance contributes to increasing the environmental sustainability of glass recycling treatment and further decrease the amount of waste to be delivered to landfilling.

References

Abukhadra M. R., Shaban M., 2019, Recycling of different solid wastes in synthesis of high‐order mesoporous silica as adsorbent for safranin dye, International Journal of Environmental Science and Technology, 16, 7573–7582

Aseel M. A., Abbas N. A., Alkaim A., 2017, Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon, Arabian Journal of Chemistry, 10, 3381-3393

Catalfamo P., Primerano P., Arrigo I., Corigliano F., 2004, Utilizzo di un residuo vetroso per la rimozione di metalli pesanti da acque reflue" Atti XIX Congresso di Merceologia Risorse Naturali e Sviluppo Economico Sociale", Vol. I, 774-779

Ghorbani F., Kamari S., 2019, Core–shell magnetic nanocomposite of Fe3O4@SiO2@NH2 as an efficient and highly recyclable adsorbent of methyl red dye from aqueous environments, Environmental Technology & Innovation 14, 100333

Hussain Z., K. Abbas, S. Nawab, A. Murad, N. Y. Muhammad, S. Khalid, S. A. Shaharin, 2019, Thermo-chemical conversion of waste glass into non-vitreous porous material for adsorption application, Journal of Material Cycles and Waste Management, Vol 21, 1132-1143

Mahmoud N. A., N. Ehssan, Husain M., 2020, Use of spent oil shale to remove methyl red dye from aqueous solutions, AIMS Materials Science, 7(3): 338–353

Mavilia L., Primerano P., Di Pasquale S., Di Bella G., Corigliano F., 2000, Il vetro post-uso come materia prima per la produzione di silicati di sodio Atti XIX Congresso di Merceologia Risorse Naturali e Sviluppo Economico Sociale, Vol. II, 209-217

Mavilia L., Primerano P., Di Pasquale S., Di Bella G., Corigliano F., 2001, Hight added value products from glass cullet Folium per l'ambiente e la Sicurezza sul lavoro, Vol. II (Suppl. al n.3) 597-603

Mohd A. A. Nur'Adilah B. A. ,Kayode A. A. ,Olugbenga S. B., 2019, Sorption studies of methyl red dye removal using lemon grass (Cymbopogon citratus),Chemical Data Collections, 22, 100249

Namasivayam C., Kavitha D., 2002, Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, Dyes and Pigments 54, 47–58

Ozbay N, Yargic AS., 2015, Factorial experimental design for Remazol Yellow dye sorption using apple pulp/apple pulp carbon–titanium dioxide co-sorbent, Journal of Cleaner Production, 333-343

Roik N. V., Belyakova L. A., Dziazko M. O., 2021, Selective sorptive removal of Methyl Red from individual and binary component solutions by mesoporous organosilicas of MCM-41 type, Journal of Environmental Sciences 99, 59-71

Song X., Wang Y., Wang K., Xu R., 2012, Low-Cost Carbon Nanospheres for Efficient Removal of Organic Dyes from Aqueous Solutions, Industrial & Engineering Chemistry Research, 13438-13444

Zoya Zaheer, Aisha AL-Asfar, Elham Shafik Aazam, 2019, Adsorption of methyl red on biogenic Ag@Fe nanocomposite adsorbent: Isotherms, kinetics and mechanisms, Journal of Molecular Liquids 283, 287–298