**PERIÓDICO TCHÊ QUÍMICA**
**ARTIGO ORIGINAL**

# ESTUDO DA ADSORÇÃO DOS CORANTES VIOLETA CRISTAL E VERDE MALAQUITA EM MATERIAL ZEOLÍTICO

# ADSORPTION STUDY OF CRYSTAL VIOLET AND MALACHITE GREEN DYES IN ZEOLITIC MATERIAL

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## RESUMO

Violeta cristal e verde malaquita são corantes utilizados na indústria têxtil. Estes compostos orgânicos são agentes tóxicos capaz de poluir recursos hídricos, bem como destruir a biota existente neste local. A descoloração de efluentes têxteis sempre foi um problema mundial, mas tem sido acentuada ao longo do tempo com a crescente operação em grande escala e mudanças na origem do uso de corantes. A descoloração das águas residuais pode ser conseguida removendo fisicamente o corante da água ou destruindo o seu grupo cromóforo. A adsorção é referida como um dos métodos mais eficientes e viáveis para descolorir um efluente. As peneiras moleculares (zeólitas) tem se mostrado uma alternativa eficiente na descoloração dos efluentes têxteis quando comparados a outros processos na indústria. A sodalita é uma zeólita que apresentar a capacidade de adsorver os grupos funcionais azo, relacionados a cor. O foco principal deste trabalho é utilizar a sodalita no processo de descoloração de uma solução sintética de violeta cristal e verde malaquita. Os experimentos foram realizados variando-se os tempos de contato entre o material zeolítico e as soluções sintética dos corantes. Os resultados nos revelaram que ambos os corantes sofreram um processo de descoloração. Conforme as análises, tempos maiores de contato (12, 24, 48 e 72 horas) com a sodalita mostra-se mais eficiente na remoção da cor. Um fator decisivo neste processo é a maior razão Si/Al (2.5) de sodalita que potencializa o processo e eficiência dos experimentos.

**Palavras-chave:** *Indústria Têxtil, Impactos Ambientais, Sodalita, Descoloração, Grupo Cromóforo*

## ABSTRACT

Violet crystal and malachite green are dyes used in the textile industry. These organic compounds are toxic agents capable of polluting water resources as well as destroying the existing biota in this location. The decolorization of textile effluents has always been a global problem, but it has accentuated over time with increasing scale operation and changes in the origin of the dyes used. Decolorization of wastewater achieved by physically removing the dye from the water or by destroying its chromophore group. Adsorption is referred to as one of the most efficient and feasible methods for discoloring an effluent. Molecular sieves (zeolites) showed to be an efficient alternative in the discoloration of textile effluents when compared to other processes in the industry. Sodalite is a zeolite that has the ability to adsorb the azo functional groups related to color. The focus of this work is to use sodalite in the process of discoloration of a synthetic solution of crystal violet and malachite green. The experiments performed by varying the contact times between the zeolitic material and the synthetic solutions of the dyes. The results revealed that both dyes had a decolorization process. According to analyzes, greater times of contact (12, 24, 48, and 72 hours) with sodalite is more efficient in the removal color. A decisive factor in this process is the higher Si/Al ratio (2.5) of sodalite that potentiates the process and efficiency of the experiments.

**Keywords**: *Textile Industry, Environmental Impacts, Sodalite, Decolorization, Chromophore Group*.

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## 1. INTRODUCTION

Pollution in aquatic systems is caused by industrial activity (Klunk *et al.,* 2017). The chemical contaminants present in the water resources are textile dyes, surfactants, and heavy metals (Klunk *et al.,* 2019a; Kumar *et al.,* 2017). These toxic agents cause the destruction of biota and changes in natural landscapes, as well as the destruction of water for human consumption (Humelnicu *et al.,* 2017). The great cause of pollution in water the textile dyes (Klunk *et al.,* 2019b). The main route of entry of the dyes into the environment is through the release of waste water. About 10 to 15 % of all dyes are directly discarded as wastewater in the dyeing process (Francis *et al.,* 2017). The first effect to be detected after illegal dumping is its aesthetic nature. At the concentration of 1 mg/L of dye, it is already enough to give color to the water resource (Chawla *et al.,* 2017). This situation makes it impossible to use water for recreational purposes and affects the natural balance of plants and other living things in the environment (Kooli *et al.,* 2015).

According to with "Ecological and Toxicological Association of Dyes and Organic Pigment Manufacturers", the majority of dyes (98 %) present lethal concentration values (LC50) in fish larger than 1 mg/L (Forgacs *et al.,* 2004). The decolorization of textile effluents has always been a global problem, but it has been accentuated over time with increasing scale operation and changes in the origin of the dyes used (Abdulrahman, 2014). As consumers become more demanding with the product (brightness, color, resistance to washing and light), the colorants become less receptive to degradation and resistant to moderate oxidation conditions (Koshy and Singh, 2016). Decolorization of wastewater can be achieved by physically removing the dye from the water or by destroying its chromophore group. Adsorption is referred to as one of the most efficient and feasible methods for discoloring an effluent (Ali, 2012; Al-Anber and Al-Anber, 2008). It is advantageous in terms of the possibility of re-use of process water, initial cost, ease of operation and insensitivity to toxic substances (Fraga *et al.,* 2014; Klunk *et al.,* 2012; Ali *et al.,* 2012; Atun *et al.,* 2011). The present work has the objective of studying the adsorption of the dye crystal violet (CV) and malachite green (MG) using molecular sieves (zeolites) as adsorbent material. For this study, standard solutions of the dyes (50 mg/L) were prepared which were contacted with the zeolitic material in the periods of 1 - 72 hours. Sodalite (zeolite) was used as adsorbent material in four Si/Al ratios (1.0, 1.5, 2.0, and 2.5). These ratios allow identifying the best adsorption condition of the dyes under study. At the end of the experiments, the products of decolorization system were analyzed by Ultraviolet - Visible Spectroscopy (UV-VIS), Fourier Transform Infrared Spectroscopy (FTIR) e High Performance Liquid Chromatography (HPLC), to verify the efficiency of the adsorbent in the removal of the color from the textile effluent.

## 2. MATERIALS AND METHODS

### 2.1. Molecular Sieves

Molecular sieves, also called zeolites, are hydrated aluminosilicates mineral of alkali metals and alkaline earths (mainly sodium, potassium, and magnesium) (Ali, 2012; Ali and Gupta, 2007). According to the International Association of Mineralogy, a zeolitic mineral is a crystalline substance with a structure characterized by structures in continuous three-dimensional crystalline networks of tetrahedral composed of four atoms of oxygen around a cation ($SiO_4$, $AlO_4$), so that each oxygen is cut between two tetrahedral (Atun *et al.,* 2011). The zeolites, in general, have structures in continuous three-dimensional crystalline networks, composed of tetrahedral of type $MO_4$ (being, M = Si, Al, Be, Ge, Fe, P, Co) (Belviso *et al.,* 2013). Due to its properties, such as the cation exchange capacity, its high surface area, its acid centers, the size of its channels and cavities and its selectivity of form 40, the natural zeolites are of great interest for the study (Koshy and Singh, 2016; Zhou *et al.,* 2014; Xie *et al.,* 2014). It should be noted that the low cost of natural zeolites has provided and stimulated the development of cheaper treatment systems (Chang and Shih, 2000; Blanchard *et al.,* 1984).

Despite having a very varied chemical composition, zeolites are usually classified according to their structure. For this study, the sodalite zeolite was synthesized and used as adsorbent material of textile dyes. Sodalite (SOD) ($Na_8Al_6Si_6O_{24}Cl_2$) was first discovered by Thomson in 1811, and after a few years in 1930, its structure was clarified by Paulling (Smith *et al.,* 2008; Smith, 2000). From this discovery, different synthesis processes were carried out to produce sodalite with the most varied compositions. The arrangement of this mineral is entirely formed by uniform truncated octahedral polyhedral, called sodalite or β-cage (Ding *et al.,* 2010; Nakano and Nozue, 2007; Bibb and Dale, 1985). Then, the α cages (supercages) with the inside diameter of

~11 Å are formed among the β cages. The α cages are connected by the sharing of the 8-membered ring with each other and also arrayed in a simple cubic structure. The lattice constant is 12.3 Å (Nakano and Nozue, 2007; Bibb and Dale, 1985).

### 2.2. Textile Dyes

Dyes are classified as anionic (acid dyes, direct and reactive), cationic (basic dyes) and nonionic (dispersive dyes) (Humelnicu *et al.,* 2017). The cationic dyes (referring to this work) present a characteristic behavior according to their concentration in solution (Almasian *et al.,* 2015). The dye molecules can bind to form molecular dimers, or even higher trimers and aggregates of the dyes (Alver *et al.,* 2012; Liu and Chiou, 2005).

In the experiments, were used the aqueous solutions of the CV and MG. The properties of the CV is cationic classification, with molecular formula $C_{25}H_{30}N_3Cl$, molecular weight 407.99 g/mol, and visible region exhibit the main peak with a maximum absorbance at $\lambda_{max}$ at 591 nm. The retention time in HPLC is 10.2 min (Al-Kadhemy and Abaas, 2012; Alsharuee, 2012). Therefore, for the dye MG, also follows in the same classification of cationic, with molecular formula $C_{23}H_{25}N_2Cl$, molecular weight 364.91 g/mol and visible region exhibit the main peak with a maximum absorbance at $\lambda_{max}$ at 620 nm. The retention time in HPLC is 4.3 min (Sartape *et al.,* 2017; Hameed and El-Khaiary, 2008).

### 2.3. Synthesis of the zeolitic material

The synthesis of zeolitic material (sodalite) was developed according to the studies of Henmi (1987). Sodium hydroxide solution was prepared by dissolving 80 g of NaOH in 1 L of distilled water. In order to obtain the zeolites with Si/Al ratio 1.0, 1.5, 2.0, and 2.5 was used as an aluminum solution, by dissolving the metakaolin ($Al_2O_3.2SiO_2$). For the Si source, biomass residue from pyrolysis experiments was used (Klunk *et al.,* 2017b; Klunk *et al.,* 2018a; Ruoso *et al.,* 2019; Cataluña *et al.,* 2018; Caetano *et al.,* 2018; Caetano *et al.,* 2015a; Caetano *et al.,* 2015b). The gel was then oven-dried at 90 °C for 24 hours. In this process, sodalite acts as an ionic adsorbent agent enable of decolorization from textile industry effluents (Klunk *et al.,* 2019c).

In environmental terms, the use of biomass contributes to the low emissions of carbon dioxide ($CO_2$) (Klunk *et al.,* 2018b; Cataluña *et al.,* 2017; Caetano *et al.,* 2015c; Caetano *et al.,* 2017). These low carbon dioxide emissions can be predicted by geochemical modeling (Klunk *et al.,* 2015; Klunk *et al.,* 2018c; Klunk *et al.,* 2019d; Ponomarev *et al.,* 2017).

### 2.4. Synthesis of the zeolitic material

In order to simulate dye contaminated effluent, was used as an aqueous solution of CV and MG (MERCK™) (Cooper, 1993). Dyes concentrations were determined by UV-visible spectrophotometry at wavelengths of 591 and 620 nm. An amount of 100 mg of adsorbent (sodalite) was placed in contact with 25 ml of a solution of adsorbate (CV and MG) at a concentration of 50 mg/L under constant stirring at 150 rpm for 24 hours (De Gisi *et al.,* 2016). After the contact time, the suspensions were centrifuged for 30 minutes at 2000 rpm, and an aliquot of the supernatant was extracted for determination of the final concentration of the dyes (Qu *et al.,* 2013).

In order to determination CV and MG color removal, 10 mL aliquots of the dyes were sampled at different periods (1, 2, 3, 4, 5, 6, 12, 24, 48 and 72 h) with 50 g of the zeolitic material (Sodalite) in different ratio Si/Al (1.0; 1.5; 2.0 and 2.5) (Klunk *et al.,* 2019c). The aqueous solution was examined by UV-Visible spectrophotometry (Ultra-Fast Scan UV-1900 - SHIMADZU™), FTIR (IRAffinity-1S - SHIMADZU™) and HPLC (LC-20A Prominence - SHIMADZU™).

## 3. RESULTS AND DISCUSSION

### 3.1. Response adsorption of CV and MG dyes in zeolitic material

In the present study, in order to follow the molecular sieve dye decolorization process, were used some analytical techniques such as UV-Vis spectroscopy, HPLC, and FTIR spectroscopy.

#### *3.1.1. Ultraviolet - Visible Spectroscopy (UV-VIS)*

UV–Vis spectroscopy is the primary technique to determine dye decolorization (Sartape *et al.,* 2017). In Figure 1, the spectra of CV and MG at a concentration of 50 mg/L in visible region exhibit the main peak with a maximum absorbance at $\lambda_{max}$ at 591 nm and 620 nm respectively (De Gisi *et al.,* 2016; Qu *et al.,* 2013). The results of the UV-Visible spectra showed that peaks at $\lambda_{max}$ reached at 0 h (FZ – free zeolite) decreased significantly until 72 h. The most efficient sodalite ratio for dye discoloration is 2.5 for both CV and MG. For the Si/Al ratio 1.0, the decolorization became less useful for the samples that remained for 72 hours in contact with the adsorbent.

### *3.1.2. High Performance Liquid Chromatography (HPLC)*

After adsorption with molecular sieve for 1, 2, 3, 4, 5, 6, 12, 24, 48 and 72 hours, the intermediates in the aqueous CV and MG solutions were extracted and analyzed via HPLC. In Figure 2, the peak at the retention time of 10.2 and 4.3 min was identified as CV and MG respectively (Cao *et al.,* 2019; Yang *et al.,* 2016; Xie *et al.,* 2013; Ayed *et al.,* 2009; Andersen *et al.,* 2009). The extracted sample after adsorption shows that decolorization is increasing according to the ratios of Si/Al increase. These values agree when comparing the results of UV-Vis spectroscopy.

### *3.1.3. Fourier Transform Infrared Spectroscopy (FTIR)*

FTIR has widely used as a proper technique for investigation of dyes decolorizations experiments. In dyes decolorization studies, FTIR spectrum enables the determination of type interactions that occur within azo dyes containing different functional groups. Taking this into account, the FTIR spectroscopy used the region of 4500-500 $cm^{-1}$ to investigate the decolorization process, and the results were shown in Figure 3 and Figure 4 to CV and MG respectively. According to the FTIR spectra, the assignments of the primary infrared bands obtained with each dye at free zeolite (FZ) and 72 h in contact with the adsorbent material in two different Si/Al ratios (1.0 and 2.5). The FTIR spectroscopy from CV have peaks at 3413 – 2921 $cm^{-1}$ indicates C-H asymmetric stretching and free $-NH_2$ group showed amide antisymmetric stretching vibration (Bevilacqua and Busca, 2002). Also, the peak at 2344 $cm^{-1}$ corresponding to a symmetric and asymmetric stretching of the tertiary amine salt. The results showed remarkable variations in ranged from 1591 - 520 $cm^{-1}$ to CV and 1650 – 545 $cm^{-1}$ to MG (Ayed *et al.,* 2009). In 1591 $cm^{-1}$ corresponding to the C=C stretching of the benzene ring. The intensity variations of 1483 $cm^{-1}$ are to six-member ring carbon-carbon vibrations and indicate a sideways ring stretch absorbs $=CH_2$. In 1361 $cm^{-1}$ peak for the C–N stretch of aromatic tertiary amine (Akyuz and Akyuz, 2006). At 1172 $cm^{-1}$ corresponds to the C–N stretching vibrations (Al-Kadhemy *et al.,* 2013). The peaks at 941, 831, 722 $cm^{-1}$ correspond to symmetric out of plane bending of the ring hydrogens. The bands at 520 $cm^{-1}$ are due to Si–O–Al (octahedral) from zeolitc material (Tyagi *et al.,* 2006).

The FTIR spectroscopy from MG have peaks at 3435 $cm^{-1}$ indicates $-NH_2$ group showed amide antisymmetric stretching vibration (Barapatre *et al.,* 2017; Vijayalakshmidevi and Muthukumar, 2013; Nishioka, 1976). The peaks at 1650 – 1400 $cm^{-1}$ is C=C aromatic ring and C–N stretch aromatic tertiary amine. Also, the peaks at 1190 and 1125 $cm^{-1}$ are for aromatic C–N stretching vibrations of aliphatic amine (Saravanakumar and Kathiresan, 2014). Eventually, the peak at 620 $cm^{-1}$ indicates aromatic amines. Bands at 545 $cm^{-1}$ were related to the internal asymmetric stretching vibration of Si-O-Si or Si-O-Al were characteristic of Sodalite structure (Cheriaa *et al.,* 2012). Among them, the band at 545 $cm^{-1}$ is related to a structure of the double five-membered rings of the pintails zeolites (Coates, 2000).

The changes in intensity variations for the dyes decolorization experiments are related to the adsorption capacity of the zeolitic as molecular sieves. According to the FTIR spectra, there was the formation of new functional groups when compared to the sample without zeolite (free zeolite). What occurred was a decrease in the intensity of the peaks. Again, the results can be compared with the other techniques used in this study, showing the same behavior.

## 4. CONCLUSIONS

The sodalite can be efficiently utilized as adsorbent for the removal of dyes (CV and MG) from aqueous solutions. In this context, the Si/Al ratios are responsible for the efficiency of the process. It was possible to identify that in the 2.5 ratios, the molecular sieve shows to be more active to adsorb both dyes (CV and MG). Soon for a reason 1.0, the process did not show us very efficiently. This discrepancy lies in the cation exchange capacity of the dyes. Thus, a low Si/Al ratio makes the molecular sieve less susceptible to the azo groups in the dye molecules. It is evident that for the three techniques used in this process of decolorization of textile dyes, the behavior of the adsorbate has the ability to retain the color related functional groups.

The zeolite used to removal the color of a textile effluent can be more efficient in the ratio Si/Al 2.5. Nevertheless, the concentration of the synthetic solution of an effluent containing CV and MG has its importance, since often the industries do a process of dilution, being able to impact in the capacity of retention of the molecular sieve.

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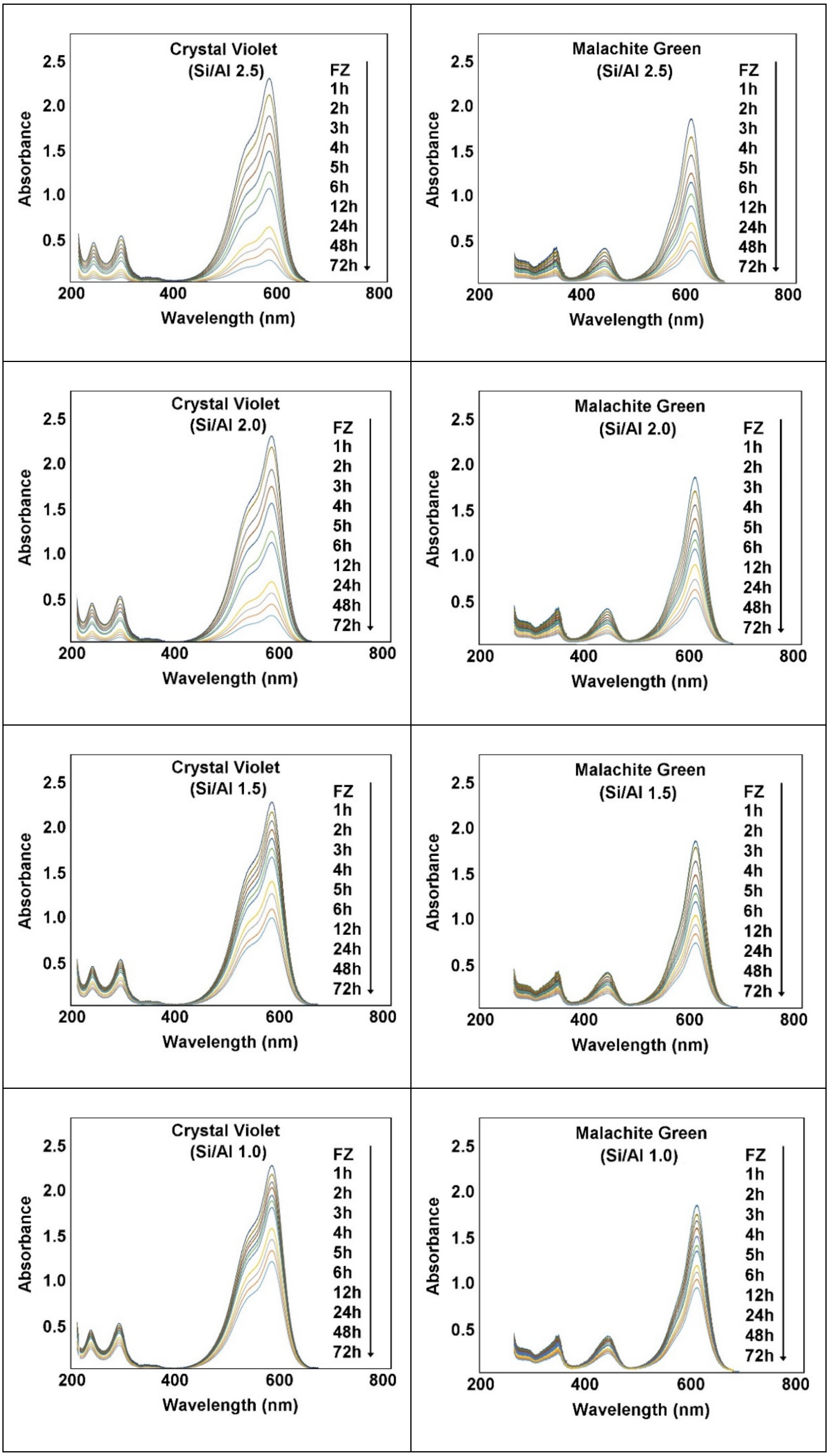

**Figure 1:** *UV-vis spectrum of CV and MG. *FZ: Free-Zeolite*

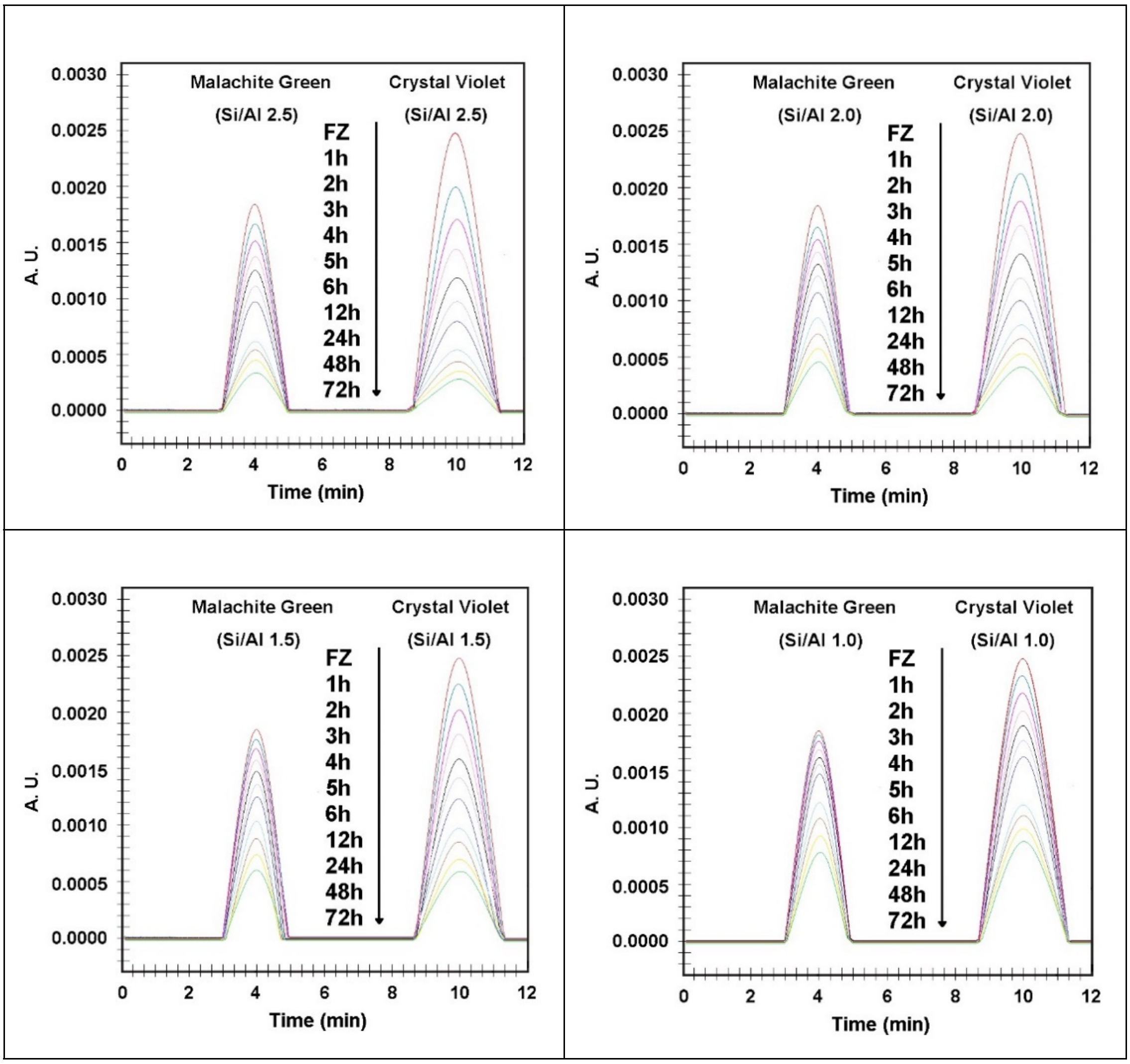

***Figure 2:*** *Chromatogram of the CV and MG of decolorization analyzed by HPLC. *FZ: Free-Zeolite*

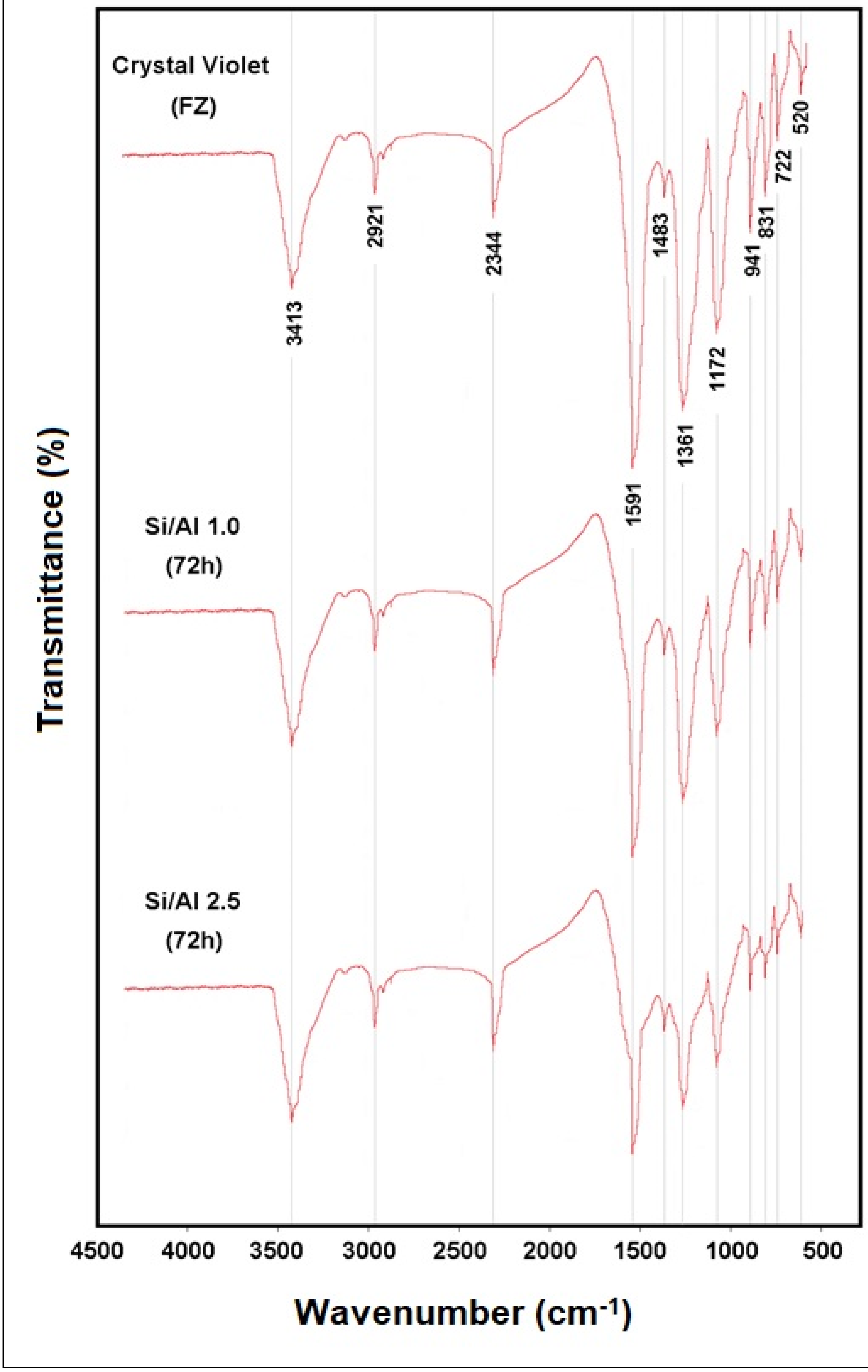

***Figure 3:*** *FTIR spectra of CV. *FZ: Free-Zeolite*

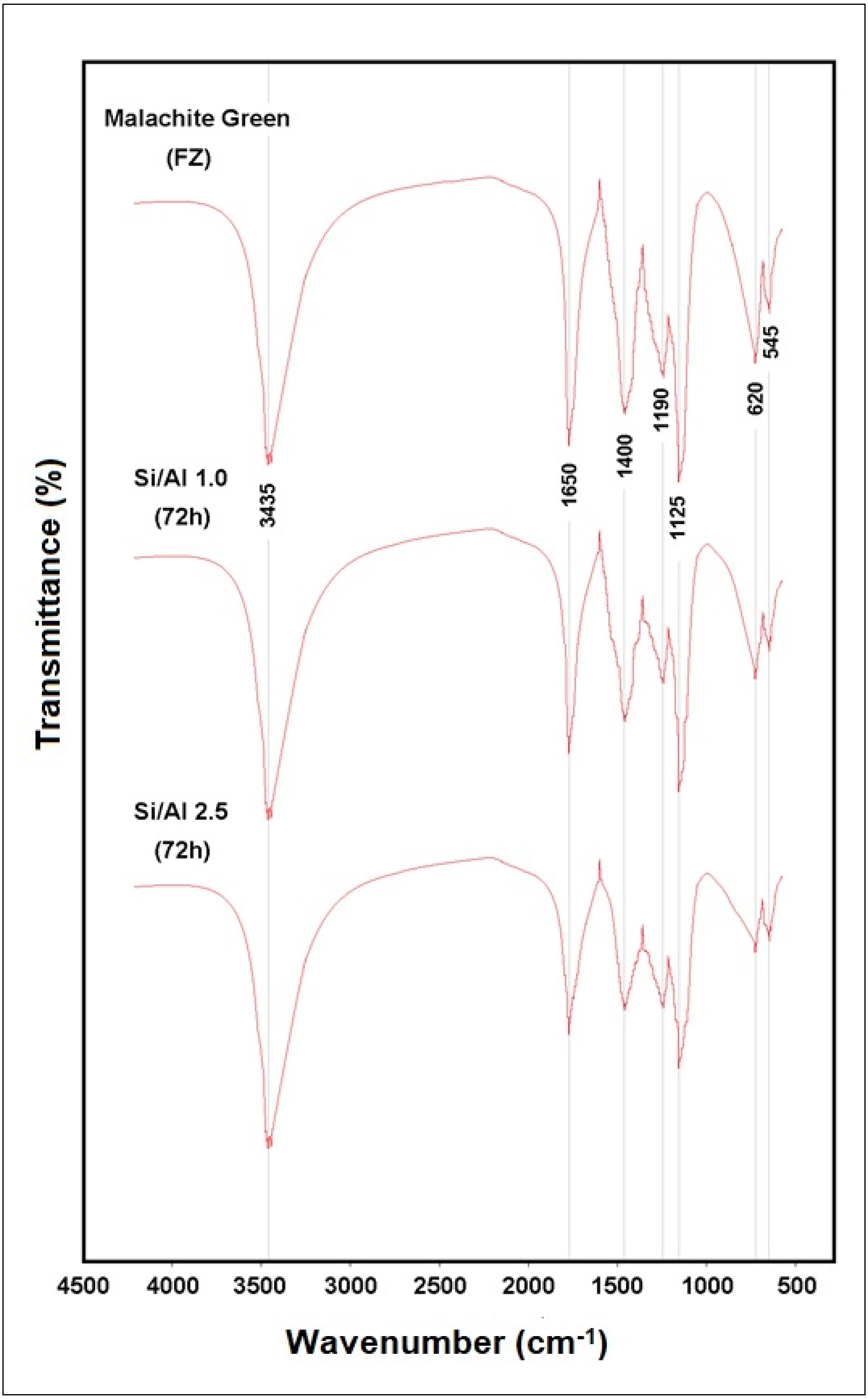

***Figure 4:*** *FTIR spectra of MG. *FZ: Free-Zeolite*