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ADSORPTION OF CRYSTAL VIOLET DYE ONTO MODIFIED ASH

BY

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Abstract. In the present study, the dye adsorption from aqueous solution, using available resources such as crystal violet as model colorant and ash/modified ash as low cost sorbent from a local power plant. The adsorbent was prepared by the alkaline method and investigated using scanning electron microscopy (SEM-EDX), X-ray diffraction (XRD) and Brunauer- Emmett - Teller (BET) methods. The adsorbent in this study had a specific surface area of 41 $m^2 \cdot g^{-1}$. The influence of several experimental conditions (initial pH, adsorbent dose, initial dye concentration, contact time) on dye removal rate was determined via batch adsorption experiments. The highest dye removal rate obtained was about 92% at pH = 10 and ambient temperature.

The results obtained in this study confirm the potential of modified ash to be used as efficient adsorbent for the removal of crystal violet dye from aqueous solution.

Keywords: modified waste ash; crystal violet dye; adsorption; factor influence; removal rate.

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1. Introduction

The dyes, natural or synthetic, are used in the textile industry pharmaceutical, paper, pulp industries etc. Textile effluents are the most representative in terms of dye pollution (Ciobanu *et al.*, 2013; Șuteu *et al.*, 2007). Dyes and their reaction products are toxic for health; their presence in effluents is of major environmental problems because they are very resistant to degradation (Helmes *et al.*, 1984; Pereira and Alves, 2012). Often, the dye solutions can form potentially carcinogenic compounds that can end up in the food chain. Wastewaters that contain dyes can block the penetration of light and oxygen, essential for life in aquatic environment. Dyes represent an important pollutant source in wastewater and the treatment of this water is very necessary for the protection of the human health and the natural environment.

Crystal violet (CV) is a basic dye very used for the coloring of paper, fibers, leather etc., but this dye is non-biodegradable and environmentally persistent (Ciobanu *et al*., 2014; Littlefield *et al*., 1985).

Recent studies are dedicated on removal of dyes from wastewater and various methods based on the adsorption, chemical, electro-chemical, physical, biological etc. processes are develop. From these methods the most important is adsorption, because result high quality water, is simple, non-toxic and is a low-cost method (Allen and Koumanova, 2005; Amodu *et al*., 2015; Buema *et al*., 2013; Rashed, 2013). The adsorption processes are based on the adsorptive properties of materials that can immobilize different pollutants from environment. As adsorbent materials can be used: activated carbon, zeolites, clay, carbonates, phosphate rocks, etc. Other types of adsorbents are wastes or by-product materials (fly ash, agriculture waste, municipal waste, coconut, banana, etc.). These adsorbents are low cost and have been extensively studied in last decade (Hernandez- Montoya *et al.*, 2013; Harja *et al.*, 2016).

Fly ash and modified ash have been used as low-cost sorbents for removal heavy metals and dyes from aqueous solutions (Harja *et al*., 2008, 2010; 2012; Ryu *et al*., 2006). Fly ash containing aluminosilicate glass, mullite, and quartz provides a ready source of Al and Si, which is necessary for the transformation of ash into zeolites. Conversion of fly ash into zeolites is based on treatment of ash with concentrated hydroxide solutions at different temperatures (Noli *et al.*, 2015; Ciocinta *et al*., 2013; Izidoro *et al*., 2012; Ojha *et al*., 2004). The methods for conversion of fly ash reported in the literature are: direct conversion, fusion, microwaves and ultrasound (Buema *et al*., 2013; Harja, 2016; Noli *et al*., 2015). In all methods, the temperature is between 20-700ºC and the contact time 4–24 h, which means energy consumption.

The present study is aimed to investigate the Crystal violet adsorption on ash and modified ash. Modified ash was obtained by direct conversion at relatively low temperature (70^0C), 5M NaOH solution, 1:3 solid/liquid ratio and 4 h the contact time. The study consists in characterization of the adsorbents and the determination of the factors affecting the adsorption, including the pH of the solutions, adsorbent dosage, dye concentration and contact time.

2. Experimental

Adsorbents characterization. The fly ash from Holboca Iași was modified by direct conversion at 70ºC, 5M NaOH solution, 1:3 solid/liquid ratio, and time of 4 h. After treatment, the synthesized samples were crystallized for 24 h at ambient temperature; filtered, washed at pH = 7 and dried.

Fly ash and modified ash were characterized by: SEM and EDAX were carried out with a Quanta 3D instrument AL99/D8229; XRD was conducted with an X'Pert PRO MRD X-ray difractometer; BET surface by nitrogen physical sorption was carried out at – 196ºC on an Autosorb 1-MP gas sorption system.

Crystal violet (CV - $C_{25}H_{30}N_3Cl$), supplied by Merck, has molecular weight of 407.98 g·mol^{-1} and is a monovalent cationic dye.

Adsorption experiments: The batch adsorption experiments were carried out by using of 200 mL initial dye solution, obtained by dilution of stock solution (1000 mg·L^{-1}) and adsorbent into reaction vessel. The pH of dye solutions was adjusted with 0.1M NaOH or 0.1M HCl and measured using a Multi-Parameter Consort C831. The samples were magnetic stirred at same rotation (300 rpm) for a given time and temperature. At establish contact time, were take samples, which after adsorbent separation were analyzed for dye concentration determination. The CV dye concentration was determined by UV-Vis device Jasco V-550 spectrophotometer at a 584 nm wavelength.

The dye adsorption capacities (q, [mg·g^{-1}]) and the removal rate (R, [%]) were calculated by means of the following equations:

$$q = \frac{C_0 - C_e}{m} V \tag{1}$$

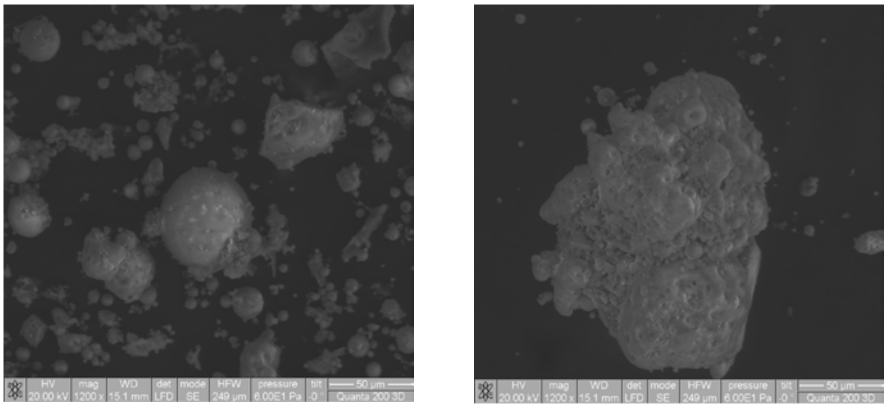
$$R = \frac{m_0 - m}{m_0}.100,\ [\%] \tag{2}$$

where: C_0 and C_e − the concentration, [mg·L^{-1}] of dye in the initial solution and at the equilibrium after the experiment; V − the volume of the solution, [L]; m − the amount of adsorbent sample used in the experiment, [g].

All experiments were run minimum three times and the average results were used to data analysis.

3. Results and Discussions

The morphology of adsorbents used in this study is presented in Fig. 1. As seen in Fig. 1, the fly ash particles are spherical, and modified ash particles are agglomerated in spherical-like shape aggregates. Sample show quite irregular and porous surfaces, with inter-granular porosity, and these indicate an adequate morphology for dye adsorption. This result is in concordance with references (Buema *et al*., 2013; El-Naggar *et al.*, 2008; Harja *et al*., 2010; Izidoro *et al*., 2012).



Fly ash Modified Ash

Fig. 1 − The SEM image of the ash and modified ash.

The specific surface area was evaluated by Brunauer-Emmett-Teller (BET) equation adsorption isotherms. Thus, the BET surface area of the ash and modified ash samples is presented in Table 1.

Table 1
The Values for Specific Surface Area, BET

Sample	S_{BET}, [$m^2 \cdot g^{-1}$]	Vpori, [$cm^3 \cdot g^{-1}$]
Fly ash	7	0.024
Modified ash	40.18	0.124

From Table 1 it can observe that by modification the specific area and volume of pores increase with over 5 times.

The adsorbents used in this study contains: Si, O, Al, Ca, Fe, K, Na, Mg and Ti, Table 2, in accord with literature (El-Naggar *et al.*, 2008; Izidoro *et al*., 2012; Javadian *et al*., 2013).

Table 2
EDAX Analysis for Adsorbents [%]

Element	O	Na	Mg	Al	Si	K	Ca	Ti	Fe
Fly ash	43.32	0.79	0.6	19.09	30.81	1.75	1.05	0.54	2.05
Modified ash	35.77	7.75	1.18	14.38	22.22	0.48	1.40	0.93	2.28

From Table 2 it was observed that in fly ash silica was present as a major component. In oxidic components the used ash was comprised of 51.2 wt.% SiO_2 and 16.9 wt.% Al_2O_3 (Harja *et al*., 2008). These elements were included in crystalline phases: calcium-aluminum silicate, quartz, and in a glass phase. Other components were also present, and confirmed by FTIR analysis (Fig. 2).

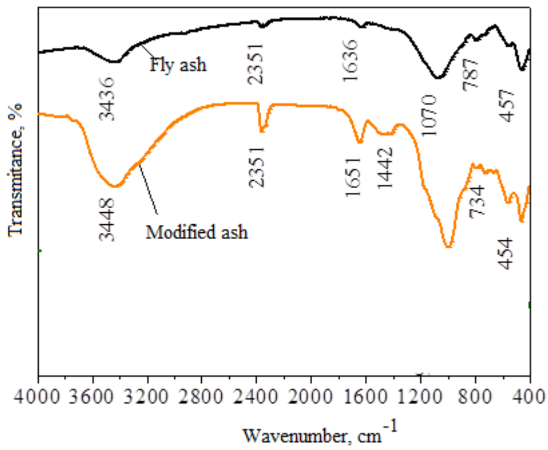
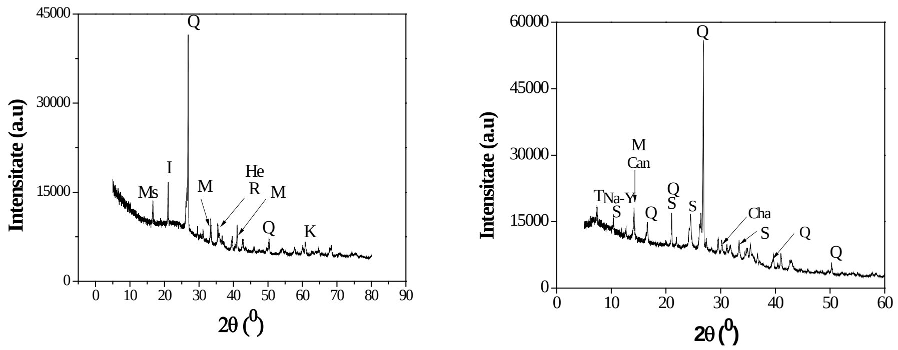


Fig. 2 − FT-IR for adsorbents.

In the spectra from Fig. 2, the relevant band was observed at 1070 cm^{-1}, corresponding to the Si/Al-O band (asymmetric stretching of O-Si-O/O-Al-O). Other picks: 457 cm^{-1} (O-Si-O bonds), 787 cm^{-1} (Si-O), 2351 cm^{-1} stretching vibrations of C=O, 1600 cm^{-1} and 3450 cm^{-1} (stretching vibrations of –OH and H-O-H). These bands correspond to quartz, mullite, hematite, kaolinite, feldspar, muscovite, sodalite (Criado *et al*., 2007; Curteanu *et al*., 2013). The existence of these minerals was demonstrated by XRD analysis (Fig. 3).



Fly ash Modified ash

Fig. 3 − X-ray diffraction patterns of ash and modified ash: A – analcime, Cha – chabazite, He – hematite, I – illite, K – kaolinite, M – mullite, Ms – muscovite, Q – quartz, S – sodalite, T – tobermorite, Na-Y zeolite.

According to Fig. 3, quartz and mullite from fly ash couldn't be completely dissolved by the hydrothermal treatment. New minerals such as: sodalite, Na-Y, tobermorite and chabazite were formed in modified sample. Literature presented that sodalite is very stable with temperature variations (Buema *et al*., 2013).

Adsorption study: In order to evaluate the CV dye adsorption ability by the ash, the effect of the pH (4-12), adsorbent dose (5-10 $g \cdot L^{-1}$), initial dye concentration (80-240 $mg \cdot L^{-1}$), and contact time (0-24 h) on the dye adsorption was studied.

Effect of initial pH: The initial pH of the aqueous solution is important in the dyes adsorption. So, the influence of the initial pH of solution on the CV dye adsorption onto studied adsorbents was determined in the pH range of 2–13 (Fig. 4), keeping all other parameters constant (initial dye concentration 80 $mg \cdot L^{-1}$, adsorbent dose 5 $g \cdot L^{-1}$, contact time 4 h and ambient temperature).

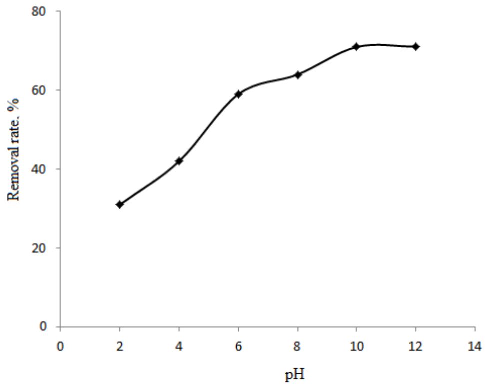


Fig. 4 − Effect of initial pH on CV dye adsorption onto fly ash sample.

The pH effect on the CV dye adsorption is related to the anionic nature of adsorbents and the cationic nature of the CV dye containing a positive amine group. The CV dye adsorption on ash and modified ash may be explained to proceed the electrostatic attraction between the negatively charged surface of the adsorbent and the positively charged group of the dye.

The highest dye removal rate was obtained at pH = 10 and ambient temperature, Fig. 5. The removal rate was about 72% for adsorption CV onto fly ash, but by modification of fly ash the removal rate increase at 95%. At high concentrations of hydrogen ion, these decreasing dye cation retention.

The high value retention, recorded at pH = 10 suggests that between ion exchange, electrostatic attraction, van der Waals interactions, is prevalent molecular interaction favored by the large size and structure of the molecule bleaching. All subsequent experiments were performed at pH = 10.

Effect of adsorbent dosage: The effect of adsorbent dosage on the removal of CV dye by the fly ash sample was evaluated over the 3-10 $g \cdot L^{-1}$ range, other parameters were constant (pH = 10, initial dye concentration 166 mg·L^{-1}, contact time 1 h and temperature 20^{o}C).

Fig. 6 shows the removal rate and adsorption capacity of dye as a function of adsorbent dosage.

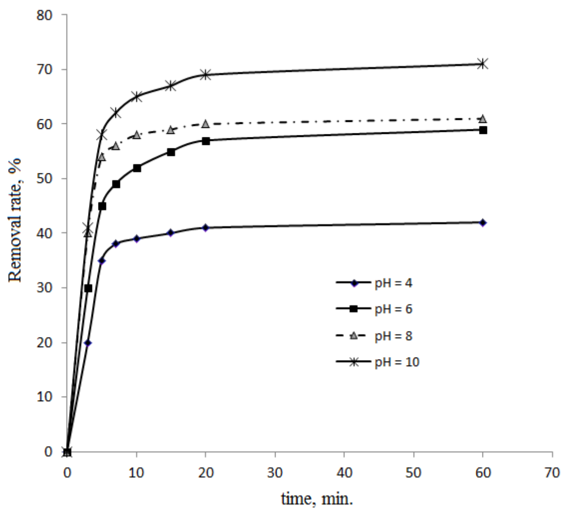


Fig. 5 ─ Influence of pH on crystal violet dye removal onto fly ash.

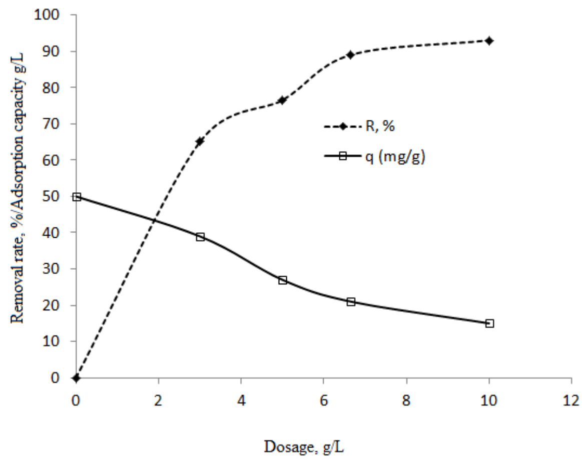


Fig. 6 ─ Effect of adsorbent dose on CV dye adsorption onto fly ash sample.

The removal rate increase with increasing adsorbent dose and the maximum (93%) was attained at 10 g·L^{-1} adsorbent dose. On the other hand, the adsorption capacity was high at low adsorbent dosages and reduced at high dosages. These results could be attributable to the increased surface area of the adsorbent and availability of more adsorption sites.

As can be seen in Fig. 7, the removal rate of CV dye decreased with the initial dye concentration. The removal rate values have maximum at the initial dye concentration of 80 $mg \cdot L^{-1}$ and modified ash as adsorbent. This indicates the fact that the adsorption reaches saturation at high dye concentration because of the adsorbent offers a limited number of surface binding sites.

Effect of contact time: The amounts of the dye adsorbed on the fly ash, respectively modified ash, sample increased rapidly in the first 30 min, then changes slightly until 1 h when the maximum adsorption is reached. After that no further adsorption occurs with prolonging time, indicating reaching an apparent equilibrium.

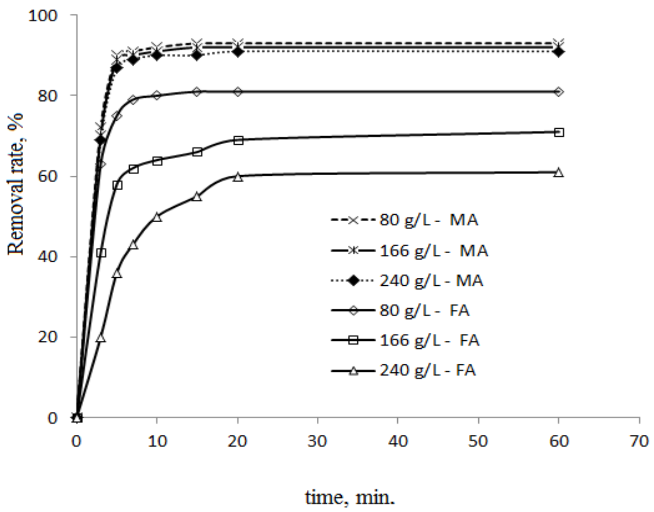


Fig. 7 ─ Effect of initial dye concentration on CV dye adsorption onto adsorbent: FA – Fly Ash, MA – Modified Ash.

The results obtained in this study suggests that fly ash and modified ash are an efficient adsorbent for the removal of CV dye from aqueous solutions, being an alternative for eliminating the CV from industrial wastewaters.

4. Conclusions

In the present paper, the fly ash has been used successfully as adsorbent for removing the Crystal violet dye from aqueous solution.

The batch adsorption experiments followed the influence of various parameters, such as pH, initial dye concentration, contact time and adsorbent dose on the adsorption process. In the batch system, the maximum dye uptake of about 93% for the modified ash. The adsorption reaction reached the equilibrium after 1 h of contact time.

The results obtained in this study indicate that the modified ash possesses good adsorption ability for Crystal Violet dye, and can be used as a low cost adsorbent for removing the dyes from wastewater.

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ADSORBŢIA COLORANTULUI CRISTAL VIOLET PE CENUȘĂ MODIFICATĂ

(Rezumat)

În lucrare se prezintă, adsorbția unui colorant - cristal violet din soluție apoasă, pe cenușă/cenușă modificată ca adsorbanţi ieftini de la o termocentrală locală. Adsorbantul a fost obținut prin metoda activării alcaline a cenușii de termocentrală, iar caracterizarea acestuia s-a realizat folosind: microscopia electronică de baleiaj (SEM-EDX), difracție de raze X (XRD) și suprafaţa specifică BET. Cenuşa modificată, utilizată ca adsorbant a avut o suprafață specifică de 41 $m^2 \cdot g^{-1}$.

Influența mai multor condiții experimentale (pH inițial, doză de adsorbant, concentrația inițială de colorant, timpul de contact) asupra gradului de îndepărtare a colorantului a fost determinată prin experimente de adsorbție. Cel mai ridicat procent de îndepărtare a fost de aproximativ 92% la pH = 10 și temperatura ambiantă.

Rezultatele obținute în acest studiu confirmă potențialul de cenușii modificate de a fi folosită ca adsorbant eficient pentru îndepărtarea cristal violetului din soluții apoase.