ADSORPTION OF DIRECT GREEN 6 DYE ONTO MODIFIED POWER PLANT ASH

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Abstract

Power plant ash and modified ash were used as the adsorbent, in this study, for the removal of textiledye direct green 6 (DG6) from aqueous solutions. The adsorbent was prepared by the alkaline attack in aqueous medium and characterized by 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 7, for power plant ash and 40 m^2g^{-1} for modified ash. Effects of various experimentalparameters, such as initialpH solution,adsorbent dosage, contact time and initial dye concentration are studied. The removal of DG6 effluent is a relatively rapid process. At pH 2 and ambient temperature, the adsorption equilibrium was reached after 4 hours and thekinetics follow a pseudo-second order model. The highest removal rate was obtained at pH 4, and was about 94% at ambient temperature. The adsorption isotherm is in goodagreement with the Langmuir model, the adsorption of dye on thesurface of new adsorbent materials was done in monolayer. The results obtained in this study confirm the potential of modified ash to be used as efficient adsorbent for the removal of direct green 6 dye from aqueous solution.

Key words: adsorption, Direct green 6 dye, modified ash, factor influence, removal rate

The present paper study the aspects of Environment & Climate Changes area, which aims at achieving of resource, protecting and sustainably managing natural and artificial resourcesand ensuring a sustainable supply and use of raw materials, in order to meet the needs of a growingglobal population within the sustainable limits of the natural resources and eco-systems. (Vinut M.*el al.,* 2017).

In the last decade the human population has increased and,consequently, this yielded in the large-scale development of the agriculture and the associated chemicalindustry, increase in resource consumption (Harper C., Snowden M, 2017).The accelerated industrial development and the societal evolution lead to serious and various environmental problems, suchas soil and water pollution, global warming,rising levels of atmospheric pollutants etc.

Chemical pollution of water is one of the major environmental problems,given that itdelays the sustainable development of both society and economy.Different contaminants are releasedinto water bodies along with the rapid industrialization (Harja M. *et al*, 2012). Dye effluent from textile industry is one ofthe most important sources of environmental pollution. Approximately 10,000 different dyes andpigments are utilized by textile industry. In the word annually are produced about 7×10^5 tons of dyes (Behnajady M.A. *et al*, 2007). Direct green 6 (DG6) is a dye very used for the coloring of paper, fibers, leather etc., but this dye is non-biodegradable and environmentally persistent.Dyes are able tocolor water even in very small concentration, as 1 ppm, theseabsorb the sunlight and reducethe photosynthetic capability of aquatic plants and microorganism (Helmes C.T. *et al*, 1984). Textile effluents are the recognized in terms of dye pollution (Ciobanu G. *et al*, 2013; Suteu D. *et al,* 2007). Dyes are toxic for health; may be cancerigenic and mutagenic, they are very resistant to degradation (PereiraL., Alves M, 2012). Dyes represent an important pollutant source in wastewater and the depollution of these is very important for the protection of the human health and the natural environment (Kant R., 2012; Rusu L. *et al*, 2014a, 2014b).

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In last years, treatment of waste water by physical and chemical methods has been the main focus (Mahmoodi N.M. *et al*, 2017; Wang G. *et al*, 2017;Yin W. *et al*, 2017).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 (Cretescu I. *et al*, 2013; Vinuth M. *et al*, 2017). From these methods the most important is adsorption, because result high quality water, is simple, non-toxic and is a low-cost method (Abdi J. *et al*, 2017;AmoduO.S.*et al*, 2015;Buema G.*et al*, 2013;MouridE. *et al*, 2017; Rashed M.N., 2013). The adsorption processes are based on the adsorptive properties of materials that can immobilize on the active centers on surface, different pollutants from water.The adsorbent materials can be: activated carbon, zeolites, clay, carbonates, phosphate rocks, etc.(Abdi J.*et al*, 2017;Ciobanu G. *et al*, 2014a; 2014b; Hernández-Montoya V.*et al*, 2013; Kaur S. *et al*, 2017; Vasugi G. et al, 2016;Ye J. *et al*, 2017). On the other hand adsorbents obtained from wastes or by-product materials (fly ash, agriculture waste, municipal waste, coconut, banana, etc.) can be used. These adsorbents are low cost and have been extensively studied in last decade (Harja M., 2016; Rashidi N.A., Yusup S, 2016; Sadegh H.*et al*, 2017).

Fly ash and modified ash have been used as low-cost sorbents for removal heavy metals and dyes from aqueous solutions (Harja M. *et al*, 2008,2010; 2011;RyuT.G. *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 F. *et al*, 2015; Ciocinta R.C.*et al*, 2013). The methods for conversion of fly ash reported in the literature are: hydrothermal method (direct conversion), fusion, microwaves and ultrasound (Buema G.*et al*, 2013;Harja M., 2016; NoliF. *et al*, 2015). In all methods, the temperature is between 20-700C and the contact time 4–24 h, which means energy consumption.

The present study is aimed to investigate the Direct Green 6adsorption onto ash and modified ash. Modified ash was obtained by hydrothermal conversion at 75C, 4M sodium hydroxide solution, 1:3 solid/liquid ratio and 4 h the contact time. The study consists in characterization of the new material and the determination of the factors affecting the adsorption, including the pH of the solutions, adsorbent dosage, dye concentration and contact time in Direct Green 6 adsorption process.

MATERIAL AND METHOD

The power plant ash, from Holboca Iasi, was modified by hydrothermal conversion at 75^{0}C, 4M NaOH solution, 1:3 solid/liquid ratio, and 4 h attack time. After modification, the samples were cooled at ambient temperature and crystallized for 18 h; after this the samples were filtered, washed at pH = 8 and dried at mass constant in oven.

All adsorbent materials were characterized by: SEM – Vega Tescan, EDAX -carried out with a Quanta 3D instrument AL99/D8229; XRD - conducted with an X'Pert PRO MRD X-ray difractometer; BET surface by nitrogen physical sorption - carried out at – 196^{0}C on an Autosorb 1-MP gas sorption system.

Direct Green 6 (DG6 - $C_{34}H_{22}N_8O_{10}S_2Na_2$) used in adsorption experiment, was supplied by Merck. The dye has molecular weight of 812.7 g mol^{-1}, the formula is presented in *figure1*:

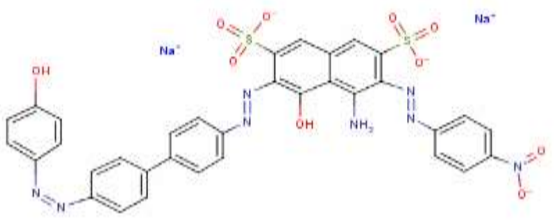


Figure.1. **Structure of Direct Green 6**

Adsorption experiments*:* The batch adsorption experiments were carried out by using of 100 mL initial solution, obtained by dilution of stock solution (100 mg L^{-1}) into reaction vessel. The pH of dye solutions was adjusted in 2-12 interval values, with 0.1 M 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 establish time and temperature. At fixed contact time were take samples which, after solid separation, were analyzed for dye concentration determination. The DG6 dye concentration was determined by UV-Vis device Jasco V-550 spectrophotometer at a 415 nm wavelength.

The dye adsorption capacities [*q*, mg·g^{-1}] and the removal rate [*R%*] was calculated by means of minimum three values, with following equations:

$$q = \frac{C_0 - C_e}{m} V \qquad (1)$$

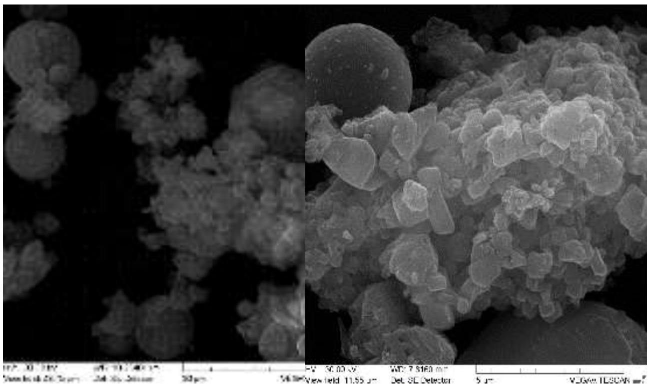
$$R\% = \frac{m_0 - m}{m_0} .100 \qquad (2)$$

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

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

RESULTS AND DISCUSSIONS

The morphology of adsorbents used in this study is presented in *figura. 2*. As seen in *figure. 2*, the power plant 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 process. This result is in concordance with references (Buema G. *et al*, 2013;Harja M. *et al*, 2010;Javadian H. *et al*, 2015).



Power plant ash Modified Ash

Figure2 **-The SEM image of the power plant ash and modified ash**

The specific surface area was evaluated by Brunauer-Emmett-Teller(BET) equation. The BET surface area of the analyzed materials samples are presented in *table 1*.

Table 1

The values for specific surface area, BET

Samples	S_{BET}, m^2g^{-1}	Vpores, cm^3g^{-1}
Power plant ash	7	0.024
Modified ash	40.18	0.124

From *table 1* it can observe that by hydrothermal treatment, 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, in accord with literature (JavadianH. *et al*,2015) and previously paper published (Harja M. *et al*, 2008, 2010).In oxidic components the adsorbents were contained: 51.2 wt.% SiO_2 and 16.9 wt.% Al_2O_3 (Harja M. *et al*, 2008). These elements were included in crystalline phases: calcium-aluminum silicate, quartz, and in a glass phase. The components from adsorbents were confirmed by FTIR analysis (*figure. 3*).

In the spectra from *figure 3*, the high 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(Curteanu S. *et al*, 2014; Harja M. *et al.*, 2009).

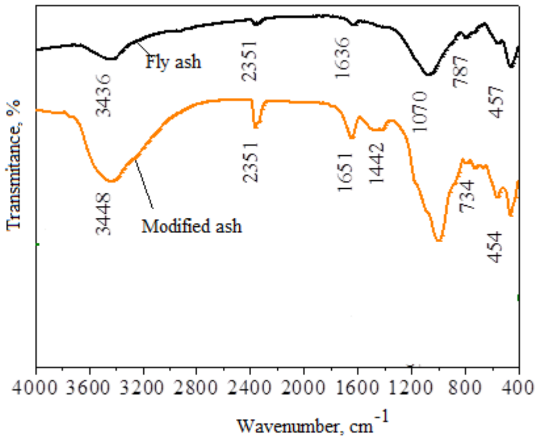
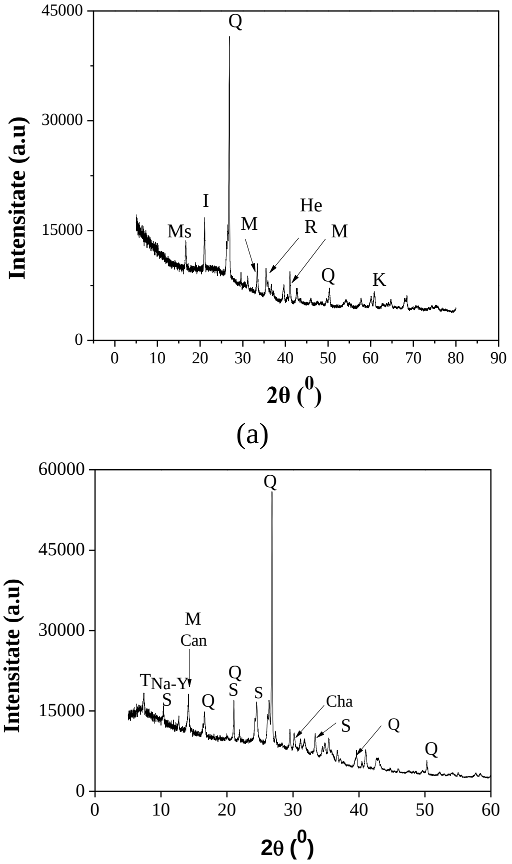


Figure3. **FT-IR for adsorbents**

The existence of these minerals was demonstrated by XRD analysis (*figure4*).



(a)

(b)

Figure4 **- 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 *figure4*, quartz and mullite from fly ash couldn't be completely dissolved by the hydrothermal treatment in relatively dilute hydroxide solution. 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 G. *et al*, 2013).

Adsorption study: In order to evaluate the DG6 dye adsorption capacity of the power plant ash, the effect of the pH (2-12), adsorbent dose (5-10 gL^{-1}), initial dye concentration (80-240 mgL^{-1}), and contact time (0-24 h) for the Direct Green 6 dye adsorption was studied.

Initial pH effect: The initial pH of the aqueous solution is very important in the dyes adsorption process. So, the influence of the initial pH of solution on the DG6 dye adsorption onto studied adsorbents was determined in the pH range of 2–12 (*figure 5*), keeping all other parameters constant (initial dye concentration 80 mgL^{-1}, adsorbent dose 5 gL^{-1}, contact time 4 h and temperature).

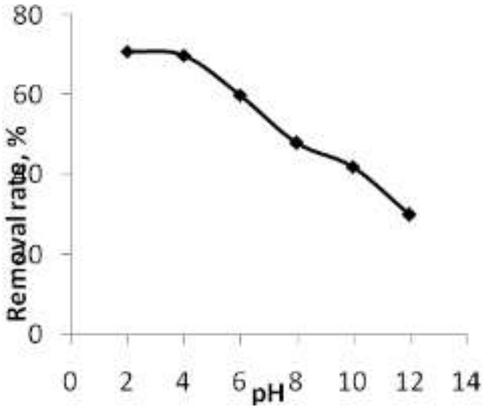


Figure5.**Effect of initial pH on DG6 dye adsorption onto power plant ash**

The pH effect on the DG6 dye adsorption is related to the cationic nature of adsorbents and the anionic nature of the DG6 dye. The DG6 dye adsorption on ash and modified ash may be explained to proceed the electrostatic attraction between the charged surface of the adsorbent and the charged group of the dye (Geetha A., Palanisamy P.N, 2014-2015).

The highest dye removal rate was obtained at pH=2 and 4 and ambient temperature, *figure 6*.

The removal rate was about 72% for adsorption DG6 onto power plant ash, but by modification of power plant ash the removal rate increase at 96%. At high concentrations of hydrogen ion, these increasing dye anionic retention.

The high value retention, recorded at pH = 4 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 = 4.

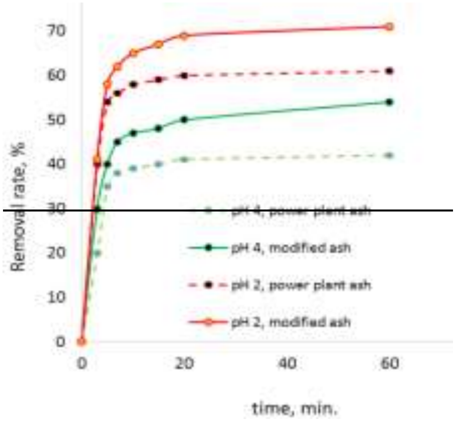


Figure6.**Influence of pH on crystal violet dye removal onto fly ash**

Adsorbent dosageeffect: The effect of adsorbent dosage on the removal of DG6 dye by the power plant ash sample was evaluated over the 3-10 g L^{-1} range, other parameters were constant (pH = 4, initial dye concentration 166 mg L^{-1}, contact time 2 h and temperature 20°C).

Figure7 shows the removal rate and adsorption capacity of dye as a function of adsorbent dosage.

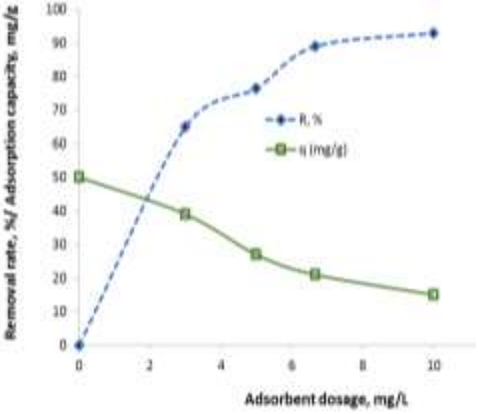


Figure7.**Effect of adsorbent dose on DG6 dye adsorption onto fly ash sample**

The removal rate increase with increasing adsorbent dose and the maximum (96%) was attained at 10 g L^{-1} adsorbent dose. On the other hand, the adsorption capacity was high at low adsorbent dosages and small at high dosages. These results could be attributable to the increased surface area of the adsorbent and availability of more adsorption sites.

Effect of initial dye concentration. As can be seen in *figure8*, the removal rate of DG6 dye decreased with the initial dye concentration. The removal rate values have maximum at the initial dye concentration of 80 mgL^{-1} and modified ash as adsorbent. This indicates the fact that the adsorption sites were saturated at high dye concentration, because at the adsorbent surface are a limited number of binding sites.

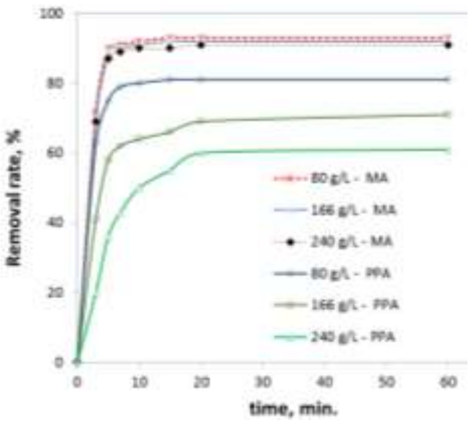


Figure 8. **Effect of initial dye concentration on DG6 dye adsorption onto adsorbent: PPA – Power Plant Ash, MA – Modified Ash**

Effect of contact time: The amounts of the dye adsorbed on the PPA, respectively modified ash, increased rapidly in the first 20 minutes, then changes slightly until 1 h when is reached the maximum adsorption value. After that no further adsorption occurs with prolonging time.

The results obtained in this study suggests that power plant ash and modified ash are efficient adsorbents for the removal of DG6 dye from aqueous solutions, being an alternative for eliminating the DG6 from textile wastewaters.

CONCLUSIONS

In the present paper, the power plant ash has been used successfully as adsorbent for removing the Direct Green 6 dye from aqueous solution.

The batch adsorption experiments followed the influence of various parameters, such as pH, initial dye concentration, contact time and adsorbent dosage on the adsorption parameters. In the batch system, the maximum dye uptake of about 96% 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 Direct Green 6dye, and can be used as a low cost adsorbent for removing the dyes from textile wastewater.

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