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REMOVAL OF MALACHITE GREEN DYE FROM AQUEOUS SOLUTIONS BY DIASPORIC GREEK RAW BAUXITE

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Abstract

Raw bauxite from Klisoura mine (Prefecture of Fokida, Greece) containing 72 wt.% diaspore, 16 wt.% hematite, 6 wt.% quartz, 4 wt.% anatase and 2 wt.% calcite, has been used for the removal of malachite green dye from aqueous solutions. The batch type experiments were conducted with 10 ml of solution, at $pH = pH_{ZPC} = 6.7$ and contact time 1 h. The initial concentration of malachite green dye was 10 mg/l, the bauxite quantity was 0.02 g, 0.04 g, 0.06 g, 0.1 g and 0.2 g. The highest adsorption capacity achieved was 4.5 mg/g (90% removal) using 0.02 g bauxite. The removal capacity of raw bauxite is comparable to other non-conventional adsorbents, such as neem sawdust, sugar cane dust and cane root carbon.

Key words: *Wastewater treatment, textile wastewater, adsorption, industrial minerals and rocks.*

Περίληψη

Ακατέργαστος ελληνικός βωξίτης από το μεταλλείο της Κλεισούρας (Νομός Φωκίδας) που περιέχει 72% κ.β. διάσπορο, 16% κ.β. αιματίτη, 6% κ.β. χαλαζία, 4% κ.β. ανατάση και 2% κ.β. ασβεστίτη, χρησιμοποιήθηκε για την απομάκρυνση της χρωστικής «πράσινο του μαλαχίτη» από υδατικά διαλύματα. Τα πειράματα τύπου batch εκτελέστηκαν σε διάλυμα 10 ml, σε $pH = pH_{ZPC} = 6,7$ και χρόνο επαφής 1 h. Η αρχική συγκέντρωση της χρωστικής «πράσινο του μαλαχίτη» ήταν 10 mg/l, ενώ οι ποσότητες του βωξίτη ήταν 0,02 g, 0,04 g, 0,06 g, 0,1 g και 0,2 g. Η μεγαλύτερη προσροφητική ικανότητα που παρατηρήθηκε ήταν 4,50 mg/g (90% απομάκρυνση) με τη χρήση 0,02 g βωξίτη. Η ικανότητα του ακατέργαστου βωξίτη στην απομάκρυνση της χρωστικής, είναι συγκρίσιμη με άλλα μη συμβατικά προσροφητικά, όπως πριονίδι από δέντρο neem, σκόνη ζαχαροκάλαμου και στάχτη ριζών καλαμιών.

Λέξεις κλειδιά: *Κατεργασία υγρών αποβλήτων, υγρά απόβλητα υφαντουργίας, προσρόφηση, βιομηχανικά ορυκτά και πετρώματα.*

1. Introduction

Removal of pollutants from wastewater is of crucial importance in environmental protection. The removal of non-biodegradable pollutants is of great interest due to their heavy potential environmental impact. Several types of industrial dyes are commonly considered as non-biodegradable pollutants. Malachite green (a N-methylated diaminotriphenyl methane) dye is a commonly used non-biodegradable industrial dye.

Malachite green dye may have serious impact on human health and the environment in general. It has been reported to cause carcinogenesis, mutagenesis, chromosomal fractures, teratogenecity and respiratory toxicity. Histopathological effects of malachite green dye include multi-organ tissue injury (Srivastava et al., 2004). Despite all these facts, malachite green dye is still in use in aquaculture and other industries, and no effective alternative to it has yet been found.

Adsorption on activated carbon has been proven to be effective in removing dyes from aqueous solutions. However, activated carbon is still considered expensive and currently the research is focused on the development of low-cost adsorbents for this purpose. Low-cost adsorbents include natural, agricultural and industrial by-product wastes. They are attractive because of their abundant availability at low or no cost and their good performance in removing dyes from aqueous solutions.

Numerous adsorbents for malachite green dye have been used. Activated carbon from pine sawdust (Akmil-Basar et al., 2005), commercially available powdered activated carbon (Kumar and Sivanesan, 2006), activated carbon from lignite (Onal et al., 2007), carbon based adsorbent from the pyrolysis of waste materials from paper industry and pine bark (Mendez et al., 2007) and bentonite (Bulut et al., 2008). A number of non-conventional sorbents (Crini, 2006) such as sugarcane dust, algae, sawdust, bottom ash, fly ash, de-oiled soya, maize cob, peat, iron humate, mixed sorbents, microbial biomass, activated slag, waste product from agriculture, magnetic nanoparticle and coal have been tested for malachite green dye adsorption: Sugar cane dust (Khattri and Singh, 1999), neem sawdust (Khattri and Singh, 2000), chemically modified rice straw (Gong et al., 2006), hen feathers (Mittal, 2006), cyclodextrin based adsorbent, (Crini et al., 2007) rubber wood (Kumar and Sivanesan, 2007), lemon peel (Kumar, 2007) and Arundo donax root carbon (Zhang et al., 2008) were also used. An extensive review on nonconventional low-cost adsorbents for dye removal was reported by Das et al. (2009). For the same purpose, surfactant modified alumina has also been used (Das et al., 2009). High quality natural zeolite have been used for the purification of dye-work wastewaters (Filippidis, 2008, 2010, 2013; Filippidis et al., 2008).

Bauxite ore may exhibit a variety of colors and is mainly composed of amorphous and/or crystalline alumina oxides and hydroxides, namely gibbsite, boemite and diaspore. It is mainly used for the production of aluminum metal. Additionally, bauxite is used for numerous non-metallurgical end uses. Through the Bayer process, bauxite is converted to alumina (Al_2O_3); especially activated alumina is used as adsorbent, desiccant and catalyst, while calcined alumina is used in abrasives, ceramics and refractories. Hard-burned (sintered) calcined alumina is used for the production of tabular alumina and principally for high performance refractory materials. Finally, fused alumina is mainly used for abrasives and refractories (e.g., Harben and Dickson, 1983; Benbow, 1988; Bolger, 1997; Crossley, 2001; Harben, 2002; Taylor, 2003).

The present study investigates, for the first time, the ability of diasporic raw bauxite (a low-cost adsorbent) to remove the malachite green dye from aqueous solutions.

2. Materials and Methods

The bauxite sample used in this study was obtained from b3 bauxitic horizon of the Klisoura open pit mine, Prefecture of Fokida, Central Greece. In the Parnassus–Ghiona geotectonic zone or Parnassus zone, three bauxitic horizons were formed, b1) Middle/Upper Jurassic, b2) Kimmeridgian/Tithonian and b3) Upper Aptian, Lower Albian, Lower Senonian (e.g., Kiskyras, 1982; Tataris, 1986).

Polished and polished thin sections of the bauxite have been studied. The mineralogical composition of the samples was determined by X-Ray Powder Diffraction (XRPD) analysis, using a

Philips diffractometer with Ni-filtered CuKα radiation on randomly oriented samples. The sample was scanned from 3° to 43° 2θ at a scanning speed of 1.2°/min. Semi-quantitative estimates of the abundance of the mineral phases were derived from the PXRD data, using the intensity (cps) of specific reflections, the density and the mass absorption coefficients for CuK_α radiation of the minerals present.

The chemical composition of the sample was measured by a Perkin Elmer 3300 Atomic Absorption Spectrometer with a graphite furnace following standard wet chemical methods. The loss of ignition (LOI) of the bauxite sample was determined gravimetrically by firing 0.8 g of the powder at 925°C for 45 min.

The raw bauxite sample was crushed by the use of agate mortar to a particle size < 63μm. Prior to the adsorption experiments the pulverized raw bauxite was dried by heating (75°C for 24 h). The pH at the potential of zero charge of the adsorbent (pH_{ZPC}) was determined using the pH drift method (Jia et al., 2002; Govindasamy et al., 2009): A solution of 0.01 M NaCl was prepared and eleven aliquots of 50 ml each were taken; their pH was fixed between 2 and 12 using 1 M HCl and 1 M NaOH solutions. In every aliquot 0.1 g of adsorbent was added and the final pH of the suspension was measured (Hanna pH 301 pH/ion meter) after 24 h.

Malachite green dye (malachitgrün-oxalat pro analysi, C.I. 42,000, FW=927.10 g/mol, Merck) was used as adsorbate, without further purification. Stock solution was prepared by diluting exactly 400 mg of malachite green dye in one litre of deionized water. The working solutions were prepared by the appropriate dilution of this solution. The adsorption of malachite green dye on natural bauxite was investigated in batch mode experiments using the standard immersion method (Rouquerol et al., 1999). For this reason, working solutions of initial concentration 10 mg/l in malachite green dye were prepared. Their pH was fixed to the desired value by using 1 M HCl and 1 M NaOH solutions. Sealing test tubes were used containing aliquots of 10 ml of solution with 0.02 g, 0.04 g, 0.06 g, 0.1 g and 0.2 g of powdered raw bauxite. They were shaken for 1 h in 20 rpm and then centrifuged in 3000 rpm for 15 min. The concentration of the remaining malachite green dye in the supernatant solution was then measured using SHIMADZU UV-1700 PharmaSpec spectrophotometer at λ=619 nm (measured value). All the adsorption studies were carried out at ambient temperature.

3. Results and Discussion

The texture of the studied bauxite sample is oolitic (Figure 1). The oolits are usually smaller than 2 mm, their shape is round or elliptic and are usually consisted of Al-minerals (diaspore) and Fe-minerals (hematite). More specifically, the oolite consists of either a mineral or mainly of concentric shells of alternating mineral composition, which indicate varying deposition conditions. Usually, either the diasporic oolits are surrounded by an outer hematite shell or hematite can be found as distinguished spots into the main mass. Finally, hematite can be found as a filling material at the rock cracks.

The XRPD analysis revealed that the bauxite sample contains 72 wt.% diaspore (theoretical chemical forlula AlOOH), 16 wt.% hematite (Fe_2O_3), 6 wt.% quartz (SiO_2), 4 wt.% anatase (TiO_2) and 2 wt.% calcite ($CaCO_3$). The mineralogical composition of the raw bauxite is in good agreement (Table 1).

The determination of pH_{ZPC} (i.e. the pH at which the mineral's surface charge becomes zero) is of great importance for bauxite, as its major mineral constituent (diaspore) encompass hydroxyl ions into their strucrure; the latter are very reactive, contributing to the total mineral electric charge. At $pH < pH_{ZPC}$ raw bauxite exhibits a net positive charge, whereas at $pH > pH_{ZPC}$ a net negative charge (Krauskopf and Bird, 1995). The studied sample demonstrates $pH_{ZPC} = 6.7$. In comparison, hematite has pH_{ZPC} between 5 and 9, goethite has pH_{ZPC} ranging around 7.5 and gibbsite has pH_{ZPC}

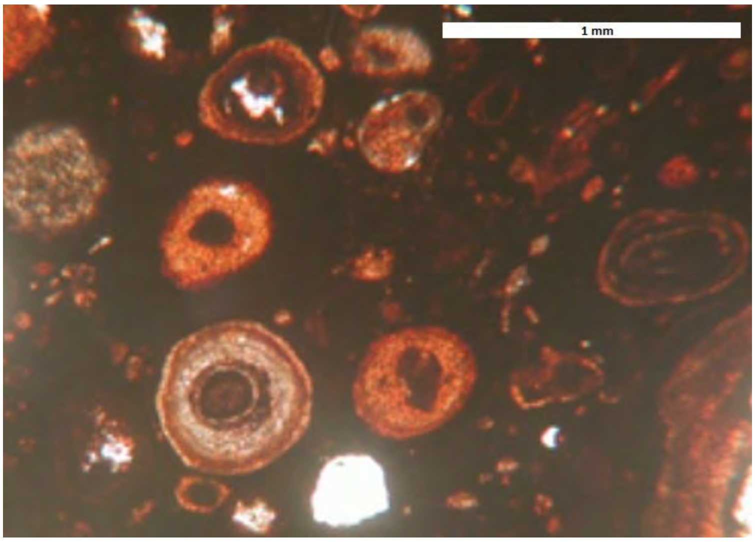

Figure 1 - Oolitic texture of the bauxite used (photomicrograph, polarizing microscope, +N).

Table 1 – Semi-quantitative mineralogical and chemical composition of the bauxite used.

Mineralogical composition (wt.%)		Chemical composition (wt.%)			
Diaspore	72	SiO_2	6.42	Na_2O	0.12
Hematite	16	Al_2O_3	59.54	TiO_2	3.84
Quartz	6	Fe_2O_3	15.16	MnO	0.01
Anatase	4	CaO	0.64	P_2O_5	0.15
Calcite	2	MgO	0.08	LOI (loss on ignition)	13.51
Total	100	K_2O	0.02	Total	99.49

= 9 (Krauskopf and Bird, 1995). For alumina a value of $pH_{ZPC} = 9.15$ and poor adsorption capacity for malachite green dye at $pH < pH_{ZPC}$ has been reported (Das et al., 2009). In general, the suspension of oxides in an aqueous solution must form distinct surface charge sites due to the following mechanism (Prado et al., 2008; Preocanin and Kallay, 2006):

$$MOH_2^+ \leftrightarrow MOH + H^+$$

$$MOH \leftrightarrow MO^- + H^+$$

and especially when hydroxyl ions are attached to aluminium cations, the following mechanism is proposed (Krauskopf and Bird, 1995):

$$Al-OH + H^+ \rightarrow Al-OH_2^+$$

$$Al-OH + OH^- \rightarrow Al-O^- + H_2O$$

The former reaction is favoured in acid solutions and the latter in basic solutions.

The effect of adsorbent dosage for malachite green dye removal at initial concentration 10 mg/l and solution $pH = pH_{ZPC} = 6.7$ is presented in Table 2 and demonstrated in Figure 3. The optimum solid to solution ratio was 0.1 g of bauxite powder to 10 ml of solution.

Table 2 – Adsorption of malachite green (MG) dye by bauxite (In all experiments: Solution volume = 10 ml, pH = 6.7 and contact time = 1 h).

Initial concentration of MG (mg/l)	Amount of bauxite added (g)	Concentration of MG after 1 h (mg/l)	Adsorption of MG (%)
10	0.2	0.36	96.4
10	0.1	0.13	98.7
10	0.06	0.15	98.5
10	0.04	0.29	97.1
10	0.02	1.00	90.0

The maximum adsorption capacity is approximately 99 % with 0.1 g and 0.06 g of bauxite per 10 ml of malachite green dye solution. This value is comparable to other non-conventional adsorbents, such as neem sawdust, sugar cane dust, hen feathers and arundo donax root carbon (Khattri and Singh, 1999, 2000; Mittal, 2006; Zhang et al., 2008).

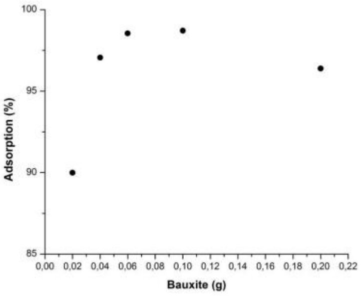

Figure 3 - Adsorption (%) of malachite green dye onto raw bauxite.

This non linear solid to solution dependence is already well documented (Limousin et al., 2007). The reasons for this effect may include, the aggregation of the suspended particles (Voice et al., 1983; Di Toro et al., 1986), the occupied volume of the suspended particles (Celorie et al., 1989), the solute transfer rate onto the surface of the adsorbent (Nandi et al., 2008) and the potential splitting of the amount of dye compounds adsorbed onto the unit weight of the adsorbent (Govindasamy et al., 2009). The optimum experimental value for solid to solution ratio for geomedia, would be a value representative of the natural conditions. The latter though demonstrate such value in general too high to be used in batch experiments (e.g. in solids the ratio tends to unity) (Limousin et al., 2007). For malachite green dye concentrations of 20 mg/l $\leq C_o \leq$ 100 mg/l, solid to solution ratio equal to 1:100 g/ml, solution pH = 5.3 ± 0.2, surfactant-modified alumina as adsorbent and at ambient temperature, the optimum time for malachite green removal was 30 min (Das et al., 2009).

In general, the decreasing order of adsorption capacities for various types of cationic dyes onto activated alumina (as amount of dye adsorbed per one gram of sorbent) is: Crystal violet > malachite green > rhodamine B > methylene blue (Singh et al., 1975). Malachite green values of $4.615 \cdot 10^{-5}$ g/g (with $k = 0.1248$ min^{-1}) and $7.590 \cdot 10^{-5}$ g/g (with $k = 0.1139$ min^{-1}) were also reported and the first order rate law for the adsorption process was found to be followed (Singh et al., 1975). The adsorption of malachite green onto surfactant-modified alumina fits into the Langmuir model isotherm, with $q_{max} = 185$ mg/g (Das et al., 2009). In this study, the maximum adsorption capacity recorded (q_{max}) was 4.5 mg/g for initial adsorbent quantity of 0.02 g.

4. Conclusions

The Greek raw bauxite as adsorbent is composed mainly of diaspore, with lesser hematite, quartz, anatase and calcite.

The adsorption capacity of diasporic raw bauxite increases up to approximately 99% for contact time 1 h, initial malachite green dye concentration 10 mg/l, solution $pH = pH_{ZPC} = 6.7$ and solution volume 10 ml. More specifically, for adsorbent dosage up to 0.06 g per 10 ml of solution, the adsorption capacity increases rapidly to 99%, then stabilizes to that value as the adsorbent amount increases up to 0.1 g and then slightly diminishes as more adsorbent is added.

The data presented, in conjunction were other literature, suggest that the phenomenon is more suitably described as a physical sorption process.

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