Removal of crystal violet from aqueous solutions using coal

Martin A. Schoonen [a,*], Jan M.T. Schoonen [a,b]

[a] Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100, United States
[b] Department of Chemical Engineering and Material Science, Stevens Institute of Technology, Hoboken, NJ 07030, United States

ARTICLE INFO

ABSTRACT

The interaction of crystal violet (CV) and six standard reference coals with varying amounts of pyrite was studied using batch sorption experiments. The experiments were designed to test the hypothesis that pyrite-containing coal removes CV through a combination of sorption and a Fenton-like degradation reaction involving pyrite. While pure pyrite does degrade CV slowly through a Fenton-like mechanism, bituminous coals containing pyrite showed far less CV removal than subbituminous coals without pyrite. Hence, the presence of pyrite in coal does not lead to an enhanced removal of CV from solution. Instead, the surface charge of coal appears to exert a primary role on the uptake of CV. The subbituminous coals tested in this study have a negative surface charge between pH 3 and 8, which facilitates the uptake of the cationic dye. Sorption of cationic CV onto subbituminous coal leads to a charge reversal. Modeling of the sorption kinetics suggest that CV diffuses into pore space within the coal after sorbing onto the surface, which is consistent with the fact that CV is not released after uptake by the coal. The results of this study indicate that subbituminous coal might be a useful sorbent for CV contained in waste streams generated in dye processes. Coal is a cheap bulk commodity, CV does not desorb easily, and the resulting CV-containing coal could be burned to incinerate the contaminant while producing energy.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Crystal violet (CV), a triarylmethane dye, is a common component in ink used in pens and printers [1]. CV and several closely related compounds are also widely used to color textile and leather. Over 100,000 different dyes are used and more than 0.7 million tons of dyes are produced annually [2]. It has been estimated that somewhere between 10% and 20% of the triarylmethane dyes are released to the environment, typically by discharge into surface waters [3,4]. Given that CV and other triarylmethane dyes are suspected carcinogens, the release of synthetic dyes represents a serious environmental problem and possible public health hazard in countries with thriving textile industries, such as India and China [1]. The coloring of surface waters with discharged dyes is also aesthetically undesirable [5].

The environmental and public health concerns have led to the development of an array of remediation strategies [2]. Most strategies rely on sorption of the dye from the process water. Several natural organic waste products, such as grapefruit peels [6], ginger

waste [7], pine bark [8], de-oiled soyabean waste [9], and palm kernel fiber and chitosan [5] have been evaluated as sorbents. The use of a wide range of agricultural solid waste to remove cationic and anionic dyes has recently been reviewed [1]. Besides agricultural solid waste, fly ash, lignite and charcoal have been evaluated as sorbents [9–11]. Other strategies rely on the degradation of the dye in the process water by microorganisms [3] or by (photo) chemical reactions. Chemical processes that have been evaluated include electrochemical degradation, photochemical degradation, reduction reactions using zero-valent iron, as well as Fenton-like, radical-based degradation [12–16]. As summarized in the recent review by Salleh and co-workers, chemical, photochemical, or microbial degradation technique have significant disadvantages and/or are costly to implement. Therefore, removal strategies based on sorption, particularly if the sorbent is a cheap bulk or waste material are of interest [9]. Chemical pretreatment of agricultural waste products to produce suitable dye sorption characteristics or the use of activated carbon adds cost. Hence, strategies based on sorption using a bulk sorbent that does not require chemical pretreatment have the lowest economic barrier to implementation.

Here we evaluate the removal of dissolved CV by coal containing various amounts of pyrite. The rationale for studying coal with different pyrite content is based on the fact that pyrite-containing

* Corresponding author. Current address: Environmental Sciences Department, Brookhaven National Laboratory, Upton, NY 11973-5000, United States. Fax: +1 6316328246.
E-mail addresses: martin.schoonen@stonybrook.edu, mschoonen@bnl.gov (M.A. Schoonen), jschoone@stevens.edu (J.M.T. Schoonen).

coal spontaneously generates hydroxyl radicals ($^\bullet$OH) when dispersed in water [17] as pyrite is oxidized by dissolved molecular oxygen [18]. The formation of OH radicals in pyrite slurries is the result of step-wise reduction of dissolved molecular oxygen at the pyrite surface [18] and has been conclusively demonstrated using Electron Spin Resonance spectroscopy [19]. We have shown that OH radicals formed in aerated pyrite slurries degrade RNA [20], DNA [19], adenine [21], and phenylanaline [22]. Independent of our studies, the same mechanism has been shown to degrade trichloroethylene [23] and lactate [24] in pyrite slurries. Because of the similarities to the classical Fenton reaction between hydrogen peroxide and dissolved ferrous iron, the formation of OH radicals in pyrite slurries has been referred to as a Fenton-like reaction [23]. Given that it is well established that CV degrades upon reaction with OH radicals [12,25–28], our hypothesis is that pyrite-containing coal removes CV from solution through a combination of sorption and degradation via a Fenton-like mechanism. Hence, the expectation is that coals containing pyrite would be superior materials to remove CV from solution compared to pyrite-free coals. Given that coal is a cheap bulk commodity it might be possible to process waters containing CV at relatively low cost. After drying, the coal powder could be burned once it is no longer effective in removing dye. Burning would effectively incinerate any sorbed CV.

Earlier work has shown that a lignite coal sorbs CV [11], but there has been no study conducted with coal reference materials of different coal rank, nor has there been a study to evaluate the use of pyrite or pyrite-containing coal to address this pollution problem. Coal rank describes the level of coalification of organic matter. It ranges from the lowest degree of coalification found in lignite, to intermediate levels found in subbituminous to bituminous coal, to the highest level found in anthracite coal [29].

2. Materials and methods

Five coal reference materials were obtained from the National Institute of Science and Technology (NIST) and one was obtained from the US Geological Survey (USGS). Full analyses of the reference materials are available on-line from NIST [30] and the USGS [31]. Table 1 provides several relevant characteristics of the coal reference materials. Included in Table 1 is the amount of OH radical formed in each of the coal slurries upon dispersion in water. These measurements were obtained in earlier work [17].

The reference materials are provided as powders and were used without any further pretreatment. The specific surface areas for the six coal reference materials were determined in earlier work using a five-point BET analysis on a Quantachrome NOVA 2000 instrument with nitrogen as adsorbate. As per instructions by the manufacturer, only measurements on at least 1 m^2 of material are reported. Hence, by using sufficient amounts of material it is possible to attain accurate specific surface area measurements on materials with less than 1 m^2/g (pers. Comm. Matthias Thommes, Quantachrome). The standard error in the BET measurement is estimated to be 2.5%. In addition to the coal reference materials, pure pyrite was used to study its interaction with CV in solution. The natural pyrite, originating from Huanzala, Peru, was obtained from Wards (Rochester, NY, USA). The material was crushed and sieved to a 63–90 micron size fraction. The specific surface area of the pyrite used in this study was 0.428 m^2/g.

A 2.46 mM primary CV stock solution was prepared by dissolving 1 g of CV in 1L deionized, ultra-filtered EasyPure™ water (hereafter abbreviated as DI). A secondary stock solution was prepared by 80-fold dilution of the primary stock solution with DI. This secondary solution (31 µM) and further dilutions of this solution were used as starting solutions in all experiments. Measurements of the

Table 1
Characteristics of coal reference materials used in study[#].

Number	Location	Coal type	Pyritic sulfur content (wt.%)	OH$^\bullet$ (24 h) (µM)
NIST #1635	Erie, Colorado	Subbituminous	0.00	0
NIST #2682b	Gillette, Wyoming	Subbituminous	0.01	0
NIST #2692b	Holden, West Virginia	Bituminous	0.49	0.3
NIST #2684b	Marion, Illinios	Bituminous	0.52	1.0
NIST #2685b	Captina, West Virginia	Bituminous	1.15	1.5
USGS CLB-1	Castleman, Maryland	Bituminous	0.67	0.4

[#] Table adapted from Cohn et al. [17]. The amount of OH$^\bullet$ generated within a period of 24 h was measured in that study using a modified 3′-(p-Aminophenyl) fluorescein assay on a coal slurry with a surface loading of 40 m^2/L [17].

absorbance of the starting solution as well as dilutions of the starting solution (1/2, 1/4, 1/10, 1/25 dilutions) using a HACH™ DR4000 UV/Vis spectrometer showed that the absorbance decreased linearly with decreasing concentration. These measurements yielded a molar extinction coefficient of 86,024 M^{-1}cm^{-1}.

2.1. Fenton degradation experiments

While there is considerable prior work to show that OH radicals generated through the Fenton reaction degrade CV [12,25–28], we conducted an experiment to determine how the visible spectra evolved over time. The experiment was conducted in a methacrylate cuvette with a 1-cm pathlength (Fischerbrand). The reaction was initiated by adding 150 µL of a 10 mM H$_2$O$_2$ solution to a mixture of 2 mL of a 10 µM CV solution and 150 µL of a 1 mM Fe^{2+} solution. After adding the hydrogen peroxide, the solution was mixed by inverting the cuvette once and then immediately place in a UV–vis spectrometer (HACH DR-4000). The solution was repeatedly scanned between 400 and 700 nm for a period of 35 min. The ferrous iron solution was prepared by dissolving ferrous ammonium sulfate salt in DI. The hydrogen peroxide solution was prepared by diluting concentrated hydrogen peroxide solution in DI. The molality of the 10 mM stock solution was checked by determining its absorbance at 240 nm.

The Fenton-CV experiment was complemented with an experiment with pyrite to investigate changes in CV spectra over time. This complementary experiment was conducted by dispersing 0.5 g pyrite in 40 mL of a 10 µM CV solution. The solution was contained in a 50 mL conical tube (Falcon™). The tube was placed on an end-over-end shaker (Labquake, Thermo Science™) and kept in the dark. Periodically, the tube was removed from the shaker, centrifuged, and 2 mL of the supernatant were pipetted out of the tube and transferred in a methacrylate cuvette. The supernatant was returned to the tube after a spectrum between 400 and 700 nm was collected. A second tube with 40 mL CV solution without pyrite was treated in the same manner for comparison. The reaction was followed for a total of 19 h (1140 min).

The initial CV concentration in the two Fenton experiments was chosen to be 10 µM after a series of preliminary experiments showed that at this initial concentration the reaction in the homogenous system proceeded at a rate that progress could be captured by consecutive scans across the 400–700 nm spectral range. The experiment with pyrite was conducted at that same initial CV concentration to be comparable to the homogeneous