

Research Article

Removal of Significant Dyes from Aqueous Solutions by means of Octolig[®]

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Abstract

Many dyes appear in our environment, including a significant number in our food supply that may need to be removed from aqueous solution. Our institute has been concerned with removal of nuisance chemicals by means of Octolig[®] a polyethylenediimine covalently attached to high-surface area silica. Collaborative research has demonstrated that a range of dyes can be removed. These include Xanthylbenzenes (Rose Bengal, Eosin Y, and Erythrosine) as well as a series of food dyes (six of the seven common food dyes) and Lissamine Green. The significance of these dyes and possibly some reasons for their removal is considered.

Introduction

Enormous quantities of chemical dyes (something over a million tons) are produced annually and used world-wide [1]. Effluents containing these materials can enter the environment through wastewater and runoffs, constituting a potential hazard. Another group of commonplace dyes are food dyes, seven of which are commonly used in the United States [2]. They have no food value, but they are added to our food, mainly to make the food more appealing. They make us feel good to eat the food, though they have no nutritional value. Moreover, they do not serve as preservatives [2].

Materials and Methods

Sources of Reagents and Materials

Octolig[®], immobilized polyethylenediimine covalently attached to high-surface-area silica gel (CAS Registry number = 404899-06-5), was a gift from Metre-General, Inc. (3771 Monarch St, Unit A, Frederick, CO 80530) and was used as received. Deionized (DI) water and tap water were available in Our Laboratory. Well water was obtained from a sprinkler attached to a shallow well aquifer at 3402 Valencia Road, Tampa, FL 33618. It was passed through fluted filter paper (802; 18.5 cm from Whatman, Inc., GE Healthcare Bio-sciences, 100 Results Way, Marlborough, MA 01752).

Column Chromatography [3-6].

A Spectra/chron peristaltic pump was used to deliver standard aqueous "Stock" samples to a CHEMGLASS chromatography column, 2 cm (id) 30 cm in length and equipped with a glass frit and a Teflon stopcock. The column was packed with a known volume of Octolig[®] resulting in a void volume of 44%. The substrate had been washed with DI water, and the supernatant, containing fines, was decanted and discarded. The procedure was repeated until no fines were noticed, then the column was packed with the washed Octolig[®].

"Stock" samples (ca.10⁻⁵M) were passed over the packed substrate using a rate of about 10 mL/min. Usually, the first four 50-mL aliquots of effluent (a.k.a. "Fractions") were discarded, and subsequent seven 50-mL fractions were used for analysis. The discard procedure was recognition of the consequences of sending a standard solution into a void volume filled with plain water. Total dissolved solids were measured using a digital conductivity meter (Fisher Scientific), and used as a guide to assess a state of equilibrium.

Other Analyses

The pH values were typically obtained using an Orion model 290A

pH/ISE meter connected with an Orion pH triode electrode model 9107BN. Concentrations of dyes in elements were acquired from the absorbance measurements using a Shimadzu UV-2401 PC UV-Vis recording spectrophotometer observed in the spectral region of 200-800 nm. Spectra were saved to a disk and analyzed using Origin Pro 8.0™.

Results and Discussion

Utilization of Octolig® In Management of Non-Food Dyes

Members of our institute have studied the removal of nuisance species by the use of Octolig®, a commercially available supported chelating agent, specifically a polyethylenediimine covalently attached to silica gel. The structure can be represented by an idealized formula: $\text{SiO}_2\text{-O-Si}(\text{CH}_3)_2(\text{CH}_2)_3\text{-NHCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_n\text{NH}_2$. Octolig® was designed as a means of removing transition metals, but our research demonstrated that it could also remove nuisance anions, including initially perchlorate [3], then simple anions phosphate, perchlorate, nitrite nitrate, as well as larger species as Zinc Phthalocyaninetetrasulfonate (ZPS) [4,5]. Dye compounds were removed successfully using Octolig®, included a series of Xanthenylbenzene dyes that included Rose Bengal, Erythrosin, and eosin. These dyes had functional groups (phenolic or carboxylic) capable of losing protons in sufficient quantities as to be capable of being converted mainly to anions and being encapsulated by attraction to protons on the nitrogens of Octolig® [5]. The three dyes in deionized water or in well water or tap water could be removed quantitatively (99.9%) by passage over a chromatography column containing Octolig®.

Effective removal of organic materials depended on compounds that existed as anions in adequate supply, e.g., those with sulfonate groups or functional groups leading to pKa values less than 4.5 [6-8]. Another example of dye management was the green dye Lissamine Green B that we demonstrated could be removed from aqueous solution by passage over a chromatography column packed with Octolig® [6]. Management in this instance would include removal from clay or other solids after the waste materials-containing the green dye had been dumped. Rosales and co-workers [1] used electro-Fenton degradation. This procedure, though effective, may be more demanding of resources, physical and personnel. We were able to demonstrate the efficacy of simple aqueous extraction, followed by removal using Octolig® [9].

An interesting alternative approach was the decolorization of textile waste water using granular activated carbon [10]. Those with memories of organic chemistry laboratory and subsequent experiences can ponder some side issues of the approach; include cost and the mess that was associated with this black powder. But "Circumstances Alter Cases" The procedure was done in Bangladesh where a supply of locally available granular activated carbon was available, as well as an adequate supply of conscientious and dedicated workers, who possibly were not supplied with rubber gloves, just as I was not.

Selected Food Dyes

At present, some seven food dyes are used in the United States, one may argue quite unnecessarily for any reasons other than aesthetics or salesmanship [2]. They do make the food more appealing. They may fool customers into believing that the food has some helpful ingredient such as fruit. The food dyes are not preservatives, nor do they make the food healthier [2]. But first and foremost, they serve a sales function. The additives make us feel good about eating the food, and having paid more than enough to cover the cost of the additive. We studied six of the seven were described in the FD&C [Food, Drug and Cosmetic Act (2938)]. These are Blue No.1 and No. 2, Green No.3, Red No. 3 and No.40, Yellow No. 5, 6 [2]. (We did not study Green No 3). At present, all seven have been used in the United States, but may question whether this is wise use of resources or wise practices.

How Useful/ How Safe Are Food Dyes?

One might argue that food dyes listed above are safe or the Food and Drug Administration would not allow the "Super Seven" to be used. The prompt answer is that all contingences can't be envisioned, though some can. Uptake of a food dye can't be guaranteed to be 100% complete. Accordingly, a problem of disposal is inevitable, though probably a problem that is ignored. The research at our institute was concerned with whether a convenient method of removal might be available, e.g., passage of a sample over a chromatography column packed with Octolig®.

There may be reason for concern, though how extensive and intensive is uncertain. For example, The Food and Drug Administration limited use of Red Dye No. 3 (January 30, 1990) because very high doses caused cancer in laboratory rats. Application of the Delany Amendment (relative to carcinogenic properties) required withdraw of authorization for use, even though the risk of getting cancer from Red Dye No 3 may have been below "1 In100,000 In A Lifetime of Consumption." By comparison, risk from natural disasters was estimated to be 70 times the quoted value [10].

Safety disagreements can arise as noted in a previous summary [11]. Yellow No. 6 (a.k.a. Sunset yellow) was especially useful for fermented foods that need to be heat treated. Margarine, Doritos, lemon gelatin deserts are among foods in this category. And though Sunset Yellow was approved by FDA, it was banned in Norway and Finland. Also, though the Center for Science in the Public Interest was convinced Blue Dye No.2 was not safe for human consumption, FDA was not, asserting results of a thorough review of pertinent literature.

Also, a case was cited of a 55-year-old man who had worked with red, yellow, and blue dyes for about ten years, but who reported adverse respiratory symptoms when exposed to Blue Dye No.2 while working, but only as a free-flowing powder [11]. Another cause for concern is a suspicion that some dyes may cause behavioral problems in some children. These problems were thought

to include aggressiveness, short-term attention spans, and impulsiveness [12]. One solution proposed was a “Feingold Diet” that excludes artificial food colorings [13]. Further studies were described earlier [11], but one must note the difficulties involved in assessing effects of food dyes on children or possibly adults.

What is the Volume of Food Dyes Used Annually?

Maybe we shouldn’t ask the question because we probably still don’t have a good answer. In 2010, The Food and Drug Administration had adequate information on the total amounts of specific batches of colors, and this was because of a requirement to provide certification. In 2010, for example, it was known that over 15 million pounds of colored batches had been certified. This value, however, covered all uses, and was, of course, different from the amount of dye used for food. As result of an earlier study, we raised the question of the incentives for knowing the amounts of dyes used for food purposes and additional specifics.

A study, reported by a Purdue group [14], indicated the consumption of food colorants was an estimated 12 mg/capita/day in 1950, but had risen to 62 mg/capita/day in 2010. The reported values varied widely with the choice of food (certain popular breakfast food versus popular energy drinks). And some suspect the levels are much higher.

Can Food Dyes Be Removed Conveniently?

We believe our research demonstrated [11] that removal from aqueous solution could be done and done quantitatively for six of the seven common food dyes. Our research indicated quantitative removal, e.g., expressed as Removal Effectiveness (Equation 1) was $99.9 \pm 0.0\%$. Removal Effectiveness = (Moles removed) x 100/ moles in stock solution - **Equation 1**

Where the \pm represents the standard deviation of the mean

Deionized (DI) water was our standard solvent, but for FD&C Red No 3 (Figure 1), tap water was also tested as a solvent, and so was well water from a shallow aquifer. FD&C Blue No 1 was removed quantitatively ($100.0 \pm 0.1\%$) as was Blue No.2 (100.0 ± 0.2).

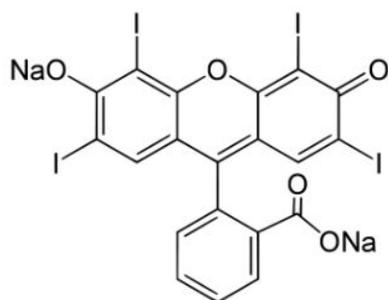


Figure 1: Structure FD&C Red No 3.

The procedure would require a compound of sufficient acidity or a suitable pH to convert the dye to an anionic species. And

the structure of Red No 3 has an aromatic carboxylic group. This is adequate for this compound for effective removal [11].

Summary

Synthetic food dyes are no doubt a valued “Articles of Commerce”, and they have aesthetic value, and perhaps psychological value. As a pre-teen during World War II living in Iowa, margarine was sold uncolored, the same color as lard. And the coloring dye came separately for suitable kneading. A younger friend “Jimmy Don” achieved certain notoriety for being able to eat bread coated with non-colored margarine. The dye didn’t add flavor, but it made the bread and spread palatable to me and others my age. Food dyes may be a small price to pay for personal comfort.

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