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Chapter 11

REMOVAL OF DYES FROM SOLUTION ON CLAY SURFACES - AN OVERVIEW

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ABSTRACT

Organic dyes are a group of those chemicals of special interest which have drawn considerable attention in many industrial processes. However due to their high toxicity and low biodegradability, various approaches such as adsorption, coagulation, sedimentation, membrane-filtration processes (nano-filtration), reverse osmosis, electrodialysis, advanced oxidation processes etc. have been forwarded concerning the removal of these dyes from solution. Adsorption is a well known equilibrium separation process and is an effective method for water decontamination applications. It is well-known that natural materials, waste materials from industry and agriculture and biosorbents can be obtained and employed as inexpensive sorbents. Some of the reported sorbents include commercially activated carbon, clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alunite, perlite) and polymeric materials as low cost adsorbents for dye removal. This overview focuses on using adsorption method to remove dyes from solution and the literature findings of such studies on various types of clays are presented.

Keywords: Clays, Dyes, Adsorption

1. INTRODUCTION

With increasing revolution in science and technology, there was a bigger demand on opting for newer chemicals which could be used in various industrial processes. Amongst the

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many chemicals used are the organic dyes. Due to the extensive use of these chemicals in industries, they have also become an integral part of industrial effluent. Most of these dyes are of diverse nature and are also potentially toxic and carcinogenic in nature and are classified as pollutants. Their removal from the industrial effluents is therefore a major environmental challenge [1, 2].

Various approaches have been forwarded to handle the removal of dyes from water. These include biodegradation, coagulation, adsorption, advanced oxidation (AOP) and the membrane process [3-8]. Table 1 outlines the various methods which are used for removing pollutants from the environment. Among these techniques, the adsorption process appears to be a promising field of study, and have been reported to be an effective tool for the removal of soluble organic contaminants from water and soil, because they can provide an almost total removal [9-20]. Adsorption is a well known equilibrium separation process. It is an effective means for water decontamination applications [21-25]. The method is cost effective, flexible in usage and simple to handle for handling the removal of different types of pollutants from the environment. Furthermore, adsorption method also does not result in the formation of harmful substances. The chemical composition and the surface properties of the adsorbents largely determine its suitability for pollutant removal. Adsorption techniques employing different solid sorbents are widely used to remove certain classes of chemical pollutants from waters, especially those that are practically unaffected by conventional biological wastewater treatments. Amongst the many solid substances used for such work are activated carbon [26-30], peat [31], resins [32, 33], polymeric substances [34-37], sand [16, 40] and clays [41-44]. This paper presents the literature findings of various researchers on the removal of dyes from solution by using different types of clays. Although the pollutant removal on clays is a vast area, the focus of attention in this work ranges within 2000- 2007 for the removal of dyes on clays.

2. EXPERIMENTAL METHODOLOGY

Different experimental techniques have been proposed for both qualitative and quantitative analysis of various types of pollutants concerning their adsorption behavior. These methods usually involve analysis by instrumental methods such as UV/Vis spectroscopy [10, 16, 45], IR [46], HPLC [47], GC/MS [48], Ion chromatography [49], Capillary Electrophoresis [50], Radiometry [51] etc. However, for adsorption studies of organic dye molecules, researches have mostly opted for spectrophotometric technique as this is easy to use for monitoring the changes in solution color before and after the experimental procedure is finished.

Table 1. Principal existing and emerging processes for dyes removal

	Methods	Advantages	Disadvantages
Conventional treatment processes	Coagulation Flocculation	Simple, economically feasible	High sludge production, handling and disposal problems.
	Biodegradation	Economically attractive, publicly acceptable treatment	Slow process, necessary to create an optimal favorable environment, maintenance and nutrition requirements
	Adsorption on activated carbons, clays etc	The most effective adsorbents, great capacity, produces a high-quality treated effluent	Ineffective against disperse and vat dyes, the regeneration is expensive and results in loss of the adsorbent, non-destructive process
Established recovery processes	Membrane separations	Removes all dye types, produce a high-quality treated effluent	High pressures, expensive, incapable of treating large volumes
	Ion-exchange	No loss of sorbent on regeneration	Not effective for disperse dyes
	Oxidation	Rapid and efficient process	High energy cost, chemicals required
Emerging removal processes	Advanced oxidation process	No sludge production, little or no consumption of chemicals	Economically unfeasible, formation of by-products, technical constraints
	Selective bioadsorbents	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, non-destructive process
	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on microorganisms	Slow process, performance depends on some external factors (pH, salts)

Ref: G. Crini, Non-conventional low-cost adsorbents for dye removal: A review, Bioresource Technology 97 (2006) 1061–1085.

3. DISCUSSION

Clays are naturally occurring substances which are well known and have been used extensively for various purposes by human beings since the early days of history. Because of their low cost, abundance in nature, and high sorption properties, clay materials have drawn a great deal of attention to be employed as adsorbents for removing pollutants from contaminated water. Additionally, clays are used in many industrial units for decontamination and color removal from various products.

The adsorption capability of a given type of clay arises from the net negative charge of the mineral. This negative charge gives clay the capability to adsorb positively charged species. The adsorption capacity depends also on the accessibility of the pollutants to the inner surface of the adsorbent, which in turn depends on their size. The high sorption properties of clays also come from their high surface area and high porosity. The large surface area of clays (upto 800 m^2/g) also contributes to their high adsorption capacity. This capacity is mainly due to their structural characteristics and their porous texture which gives them a large surface area. Besides this, the chemical nature of clays can be easily modified by chemical treatment in order to increase their properties.

3.1. Characteristics of Clays [52-57]

Clay mineral is a layer silicate mineral (also called a phyllosilicate) or other mineral which imparts plasticity and which hardens upon drying or firing. The basic structure of the phyllosilicates is based on interconnected six member rings of SiO_4^{-4} tetrahedra that extend outward in infinite sheets. Three out of the 4 oxygens from each tetrahedra are shared with other tetrahedra. This leads to a basic structural unit of $Si_2O_5^{-2}$. Figure 1 shows the structure of phyllosilicate. Clay materials are classified by the differences in their layered structures. There are several classes of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite. This section briefly describes the essential characteristics of those clays which are generally used for adsorption purposes.

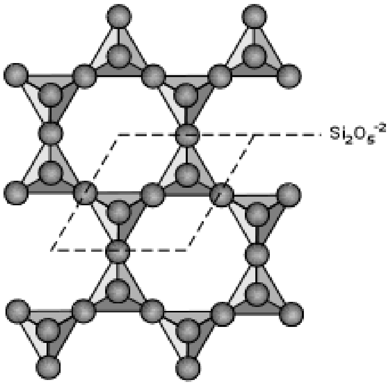


Figure 1. The basic structure of phyllosilicates.

a) Smectites

These are a family of clays that swell when immersed in water or some organic liquids (those which, like water, have polar molecules). Formerly they were known as the montmorillonite group; that name is now only used for one mineral in the smectite group. All smectites have very high cation exchange capacity (of the order of 1000 meq/kg = 1 mmole of positive charge per gram). Smectites are 2:1 phyllosilicates with total layer charge between 0.2 to 0.6 negative charges per half unit cell layer. This group was formerly called the Montmorillonite group, but the name was changed in the 1970s to avoid confusion because the name montmorillonite also refers to an individual species of smectite. Their structure is very similar to that of the other 2:1 phyllosilicates except that the total layer charge is 0.2 - 0.6 negative charges per half unit cell layer and they are typically hydrated. Because of this permanent charge, smectite interlayers always contain cations to provide electro neutrality. These cations are generally available to participate in cation exchange reactions unless they are large polyanions of aluminum or iron.

In hydrated smectites, the superposition of one layer over another is not controlled by the presence of K in the ditrigonal holes, as in micas, nor by the hydrogen bonding of one layer to another, as in the kandites. This lack of layer-to-layer rotational limitation produces a condition called as turbostratic stacking, wherein any one layer may assume any degree of rotational orientation with respect to the layers above and below it. Lateral movement of one layer with respect to another is also not limited. Because of this lack of orientation, one cannot describe all the stacking symmetry of smectite layers in any idealized unit cell. Thus, smectites are not true minerals, but rather para-minerals or paracrystalline minerals.

b) Montmorillonite

Montmorillonite is a very soft phyllosilicate mineral that typically forms in microscopic crystals, forming clay. Montmorillonite, a member of the smectite family, is 2:1 clay, meaning that it has 2 tetrahedral sheets sandwiching a central octahedral sheet. A representative structure of this clay is shown in figure 2. The particles are plate-shaped with an average diameter of approximately 1 micrometre. It is the main constituent of the volcanic ash weathering product, bentonite. Montmorillonite's water content is variable and it increases greatly in volume when it absorbs water. Chemically it is hydrated sodium calcium aluminium magnesium silicate hydroxide $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$. Potassium, iron, and other cations are common substitutes, the exact ratio of cations varies with source. It often occurs intermixed with chlorite, muscovite, illite, cookeite and kaolinite.

c) Bentonite

Bentonite is an absorbent aluminium phyllosilicate, generally an impure clay consisting mostly of montmorillonite. When bentonite absorbs water and swells, it is stretched open like a highly porous sponge; the toxins are drawn into these spaces by electrical attraction and bound fast. In fact bentonite can absorb pathogenic viruses, aflatoxin (a mold), and pesticides and herbicides. There are a few types of bentonites and their names depend on the dominant elements, such as K, Na, Ca, and Al. As noted in several places in the geologic literature, there are some nomenclatorial problems with the classification of bentonite clays. Bentonite usually forms from weathering of volcanic ash, most often in the presence of water. However, the term bentonite, as well as a similar clay called tonstein, has been used as clay beds of uncertain origin. For industrial purposes, two main classes of bentonite exist: sodium and calcium bentonite. In stratigraphy and tephrochronology, completely devitrified (weathered volcanic glass) ash-fall beds are commonly referred to as K-bentonites when the dominant clay species is illite.

d) Kaolinite

Kaolinite is a 1:1 aluminosilicate consisting of stacked pairs of tetrahedral silica sheets and octahedral alumina sheets. Each pair of sheets is bound together through common oxygen atoms, and successive pairs are held together by hydrogen bonding between Si-O and Al-OH groups. The resulting crystal has a silica face of SiO_2 tetrahedra, an alumina face carrying AlOH groups, and edges which carry both SiOH and AlOH sites. The general formula of Kaolinite is $Al_2[(OH)_2|Si_2O_5]$ and its crystal structure is shown in figure 3.Under normal conditions kaolinite does not swell because of the strong hydrogen bonding between the 1:1 pairs. Isomorphous substitution in the silica layer leaves that face with a small permanent negative charge, while the charge on the alumina face and on the edges is pH-dependent. The point of zero charge (pzc) of kaolinite is approximately 4–4.7.

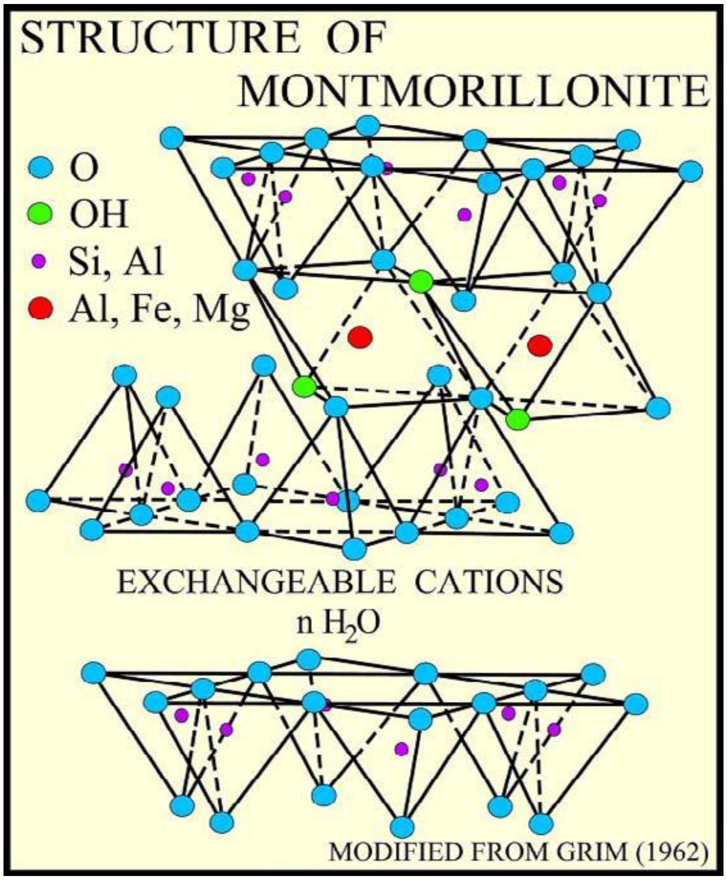


Figure 2. Structure of Montmorillonite.

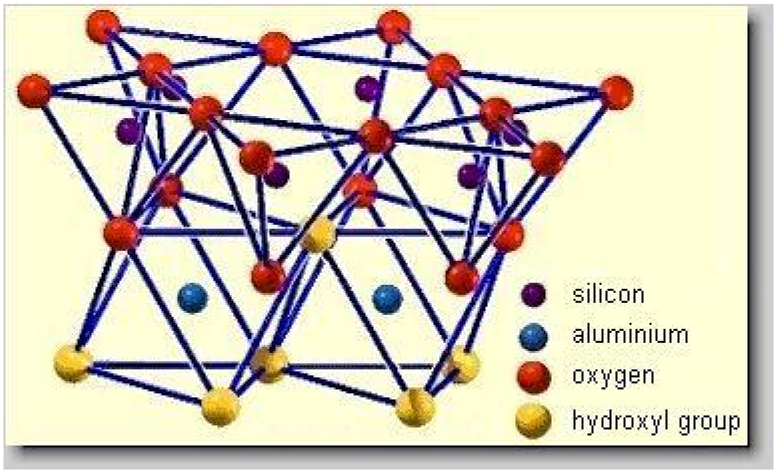


Figure 3. Crystal lattice of kaolinite. Kaolinite consists of an octahedron layer (coordinates around Al) and a tetrahedron layer (coordinates around Si).

The strongest preference for kaolinite is shown by polyaromatic molecules carrying amino groups. Such solutes can associate by pi-stacking, and could also interact with the permanent negative charges on the flat silica faces of the kaolinite crystals. The extent of adsorption of the solutes to the edges of kaolinite crystals is probably much the same as that to the oxides, because the kaolinite edges are structurally similar to the oxide surfaces.

e) Diatomite

Diatomite is a powdery, non-metallic mineral composed of the fossilised skeletal remains of microscopic single-celled aquatic plants called diatoms. Over 10,000 species of these microscopic algae have been recognized, each with its own distinct shape, ranging in size

from under 5 microns to over 100 microns. Diatomite deposits are usually categorized based upon their fresh water or salt water origin. Both the chemical composition and the physical structure of diatomite make it of great commercial value for a wide spectrum of uses, including filter aids, functional fillers, carriers for active ingredients and diluents, and aggregates. Diatoms have the unique ability to absorb water-soluble silica present in their natural environment to form a highly porous, yet rigid, skeletal framework of amorphous silica.

f) Fuller's Earth

It is composed mainly of alumina, silica, iron oxides, lime, magnesia, and water, in extremely variable proportions, and is generally classified as sedimentary clay. The mineral generally contains montmorillonite or palygorskite (attapulgite) or a mixture of the two; some of the other minerals that may be present in fuller's earth deposits are calcite, dolomite, and quartz. Fuller's earth is any nonplastic clay or claylike earthy material that can be used to decolorize, filter, and purify animal, mineral, and vegetable oils and greases. It is characterized by its property of absorbing basic colors and removing them from oils.

g) Sepiolite

Sepiolite is a clay mineral with a typical formula of $Mg_4Si_6O_{15}(OH)_2 \bullet 6H_2O$. Removal of the structural water causes the sepiolite crystals to fold by rotation of the fibers on axes through the inverted Si-O-Si edge bonds, thus, allowing the terminal Mg^{2+} to complete their coordination with the oxide surface of the neighboring silica layer.

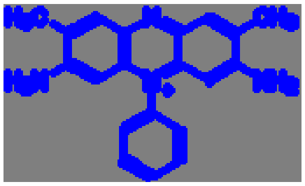
The thermal behavior of sepiolite has shown that the structural changes of the material with increasing temperature affect the specific surface area and its adsorption capacity. Sepiolite has structurally four water molecules coordinated to magnesium. The loss of these water molecules with increasing temperature will affect the specific surface area and adsorption capacity of sepiolite. It has been known that water molecules coordinated to magnesium lose until 500^0C. After loosing four water molecules which are coordinated to magnesium, the structure folds. Structural folding is associated with a decrease in the adsorption properties since the channels become narrower and the superficial slots sinter. A further increase in temperature produces the dehydroxylation of the structure and leads to the formation of clinoenstatite [57].

h) Zeolites

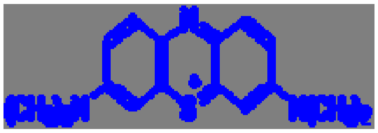
Compositionally, zeolites are similar to clay minerals. More specifically, both are alumino-silicates. They differ, however, in their crystalline structure. Clays have a layered crystalline structure (similar to a deck of cards) and are subject to shrinking and swelling as water is absorbed and removed between the layers. In contrast, zeolites have a rigid, 3-dimensional crystalline structure (similar to a honeycomb) consisting of a network of interconnected tunnels and cages. Water moves freely in and out of these pores but the zeolite framework remains rigid. The zeolites are framework silicates consisting of interlocking tetrahedrons of SiO_4 and AlO_4. In order to be a zeolite the ratio (Si +Al)/O must equal 1/2. The alumino-silicate structure is negatively charged and attracts the positive cations that reside within. Zeolites have an open structure that can accommodate a wide variety of cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+} and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Zeolites have high cation exchange capacity (CEC) which arises during the formation of the zeolite from the substitution of an aluminum ion for a silicon ion in a portion of the silicate framework (tetrahedral units that make up the zeolite crystal). More than 150 zeolite types have been synthesized and 48 naturally occurring zeolites are known. Some of the more common mineral zeolites are: analcime, chabazite, heulandite, natrolite, phillipsite, and stilbite. An example mineral formula is: $Na_2Al_2Si_3O_{10}$-$2H_2O$, the formula for natrolite.

3.2. Adsorption of Dyes

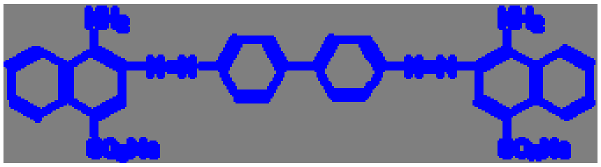
Suitable clay should possess not only a porous texture, but also high surface area. The adsorption does not always increase with surface area. Besides the physical structure, the adsorption capacity of given clay is strongly influenced by the chemical nature of the surface. The acid and base character of clay influences the nature of the dye isotherms. The adsorption capacity depends also on the accessibility of the pollutants to the inner surface of the adsorbent, which depends on their size. The specific sorption mechanisms by which the adsorption of dyes takes place on these adsorbents are still not clear. This is because adsorption is a complicated process depending on several interactions such as electrostatic and non-electrostatic (hydrophobic) interactions. Clays show strong adsorption behavior for both heteroatomic cationic and anionic dyes. Figure 4 shows the chemical structures of some dyes. The clays usually have high sorption capacity for dyes; this property is well known for both acidic and basic dyes [58-61].However, the sorption capacity for basic dye is much higher than for acid dye because of the ionic charges on the dyes and characteristic properties of the clay. Since the sorption capacity also depends on the surface area of the adsorbent, the higher the surface area the more adsorption will take place.



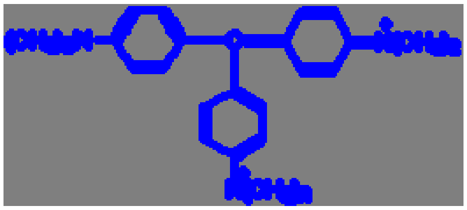
Basic Red 2 (Safranin O)



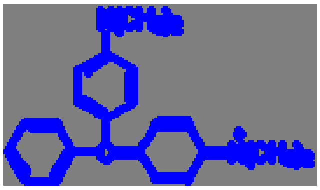
Basic Blue 9 (Methylene Blue)



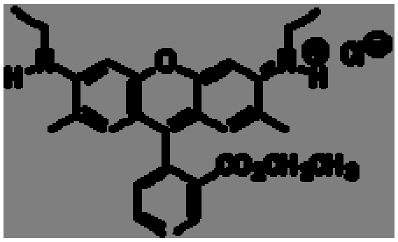
Congo Red



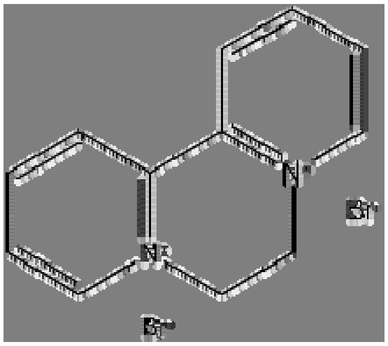
Methyl Green



Malachite Green

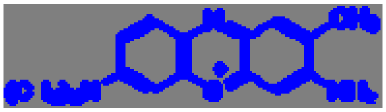


Rhodamine 6G

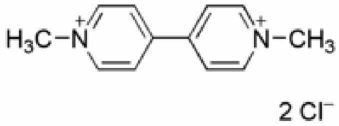


Diquat

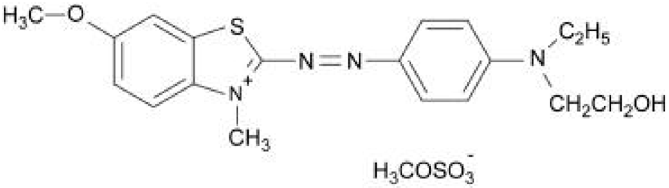
Figure 4. (Continued)



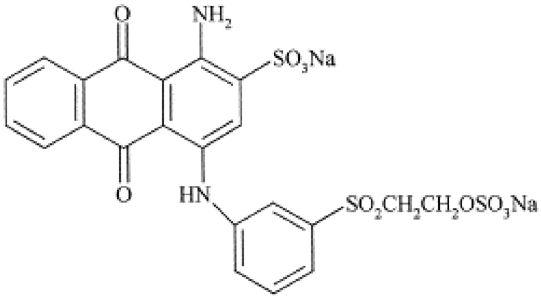
Toludine Blue O



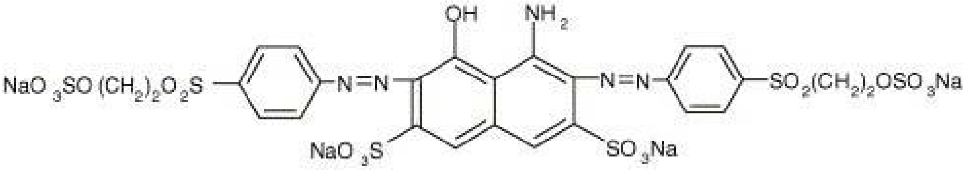
Paraquat



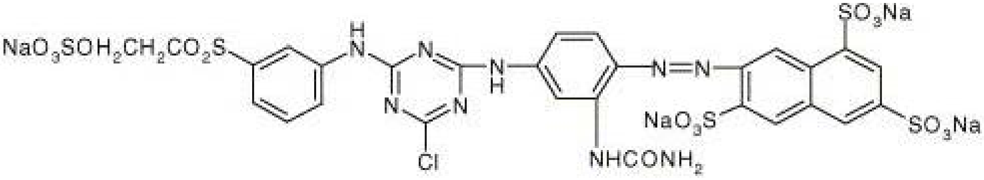
Basic Blue 41



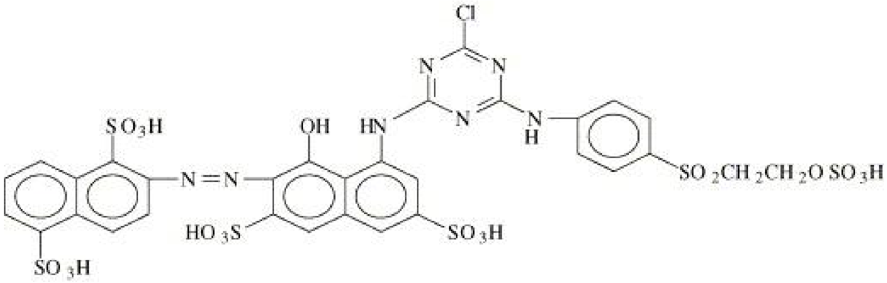
Reactive Blue 19



(a) Reactive Black 5 (RB5)



(b) Reactive Yellow 145 (RY145)



Reactive Red 239

Figure 4. Chemical Structures of some dyes.

Due to the high surface area of bentonite, it has been suggested to be a good adsorbent for (basic) dye removal. An adsorption capacity of 300-360.5 mg of dye/g bentonite has been reported in the literature [62,63]. The adsorption kinetic studies of the adsorption of a commercial dye, Basic Red 2 (BR2) on bentonite from an aqueous solution showed that the removal of BR2 was a rapid process and the adsorption process obeyed the pseudo-second-order model, indicating cationic dye had a very strong affinity on the bentonite surface and had a very high BR2 adsorption capacity of approximately 274 mg/g at 30^0C [64]. Modification of bentonite surface has shown improvement in its sorption capacity. The acid-treated bentonite showed a higher adsorption capacity than non-modified bentonite [63]. Bentonite surface modified by a surfactant has shown a sorption capacity of 206.6 mg/g of the Reactive Blue 19 [65]. Enhanced sorption capacity of bentonite has also been reported by other researchers upon modification of the adsorbent surface [66, 67]. Increasing the ionic strength increased the adsorption of Crystal violet (a basic dye) onto bentonite samples. The adsorption capacities of the cation-saturated bentonites were higher than that of the raw and acid activated bentonite. Likewise the adsorption capacity of Acid Red 151 has been found to be 357.14 and 416.66 mg/g for the cetyldimethylbenzylammonium chloride-bentonite (CDBA-bent) and cetylpyridinium chloride-bentonite (CP-bent), respectively [68].

The adsorption of dyes on kaolinite has not been studied widely. There are only a few reports on its use as an adsorbent for dyes [55,69]. In the case of methylene blue adsorption studies on kaolinite, it was shown that the dye adsorbed more to the surface under basic conditions [69]. The increased adsorption in basic conditions was related to preferential affinity of the dye cations for basic sites. In aqueous medium, the exchangeable alkali and other metal cations on the surface and in the interlayer region of the clay undergo hydration creating a hydrophilic environment. Increasing the pH of the adsorbing medium modifies the clay mineral surface thus increasing the adsorption of methylene blue.

Montmorillonite clays have the smallest crystals, the largest surface area and the highest cation exchange capacity. Thus montmorillonite clays would be expected to have the highest sorptive capacity. Due to its salient characteristics the clay has been used for removing dyes from solution as shown in many studies [70-77]. The behavior of adsorption of the cationic dye C.I. Basic Blue 41 onto montmorillonite, bentonite, raw perlite, and expanded perlite has been reported in the literature [78] and it was found that the dye molecules interact with each other as well as with the acidic sites of the silicate surface for all nano-adsorbents used. The H aggregates was found to be formed at the nano-adsorbents surfaces and transferred to dye monomers, dimers, and J-aggregates. This is then followed by migration into the interlamellar space resulting in intercalation of the clay even at low dye loadings. The dye molecules between the silicate sheets may adopt different orientations and, eventually become layered depending on the dye loading and the temperature.

The removal of xanthene basic dye, Rhodamine 6G [79], disazo acid dye, Amido black 10B (C.I. 20470) [80], and disazo acid dye, Methyl Orange 52 (C.I. 13025) [81], by HCl-activated montmorillonite in fixed beds, is also reported in the literature. It was found that the adsorption capacity of acid dye onto raw clay could be largely improved when the clay was activated by HCl. The increase of adsorption capacity was attributed to the replacement of Al^{3+} or Fe^{2+} ions of montmorillonite by H^+ ion after HCl acidification. The nano-clay, montmorillonite, and some modified nanoclays have also been used as sorbents for nonionic, anionic and cationic dyes [81]. The nanoclay showed a sorption of 90% at an initial dye concentration of 6 g/L, or 60% based on the weight of the sorbent, indicating an extremely high dye affinity.

Polymer/layered silicate nanocomposites frequently exhibit remarkably improved mechanical and materials properties and are attracting considerable interest in polymer science field [44]. The adsorption of tannic acid, humic acid, and some dyes (methylene blue, reactive dye RR222) from water using the composite of CTS and activated clay has also been reported in the literature [82]. Likewise adsorption of Congo Red dye on chitosan/montmorillonite nanocomposite (CTS/MMT) is also reported [44]. The adsorption kinetics obeyed the pseudo-second order model, and the isotherm followed the Langmuir monolayer model. Compared with chitosan(CTS), the CTS/MMT nanocomposite has a good flocculation ability in aqueous solution, comparative low cost and relative high adsorption capacity. Therefore, this nanocomposite was found to be an effective adsorbent for the removal of dyes from wastewaters.

Fuller's earth (FE) has also been reported as a potential adsorbent for the removal of dyes

The adsorption studies of methylene blue on FE has shown that the adsorption process is very fast compared to that on activated carbon and also that FE samples have higher adsorption capacity in the range of 3 x 10^{-4} to 6.0 x 10^{-4} mol/g at 298 K [83]. Adsorption characteristics of Toluidine Blue (TB) on nontreated clay were compared with those obtained for acid and alkaline-treated samples [84]. It was found that the adsorption capacity of alkali treated Fuller's earth is higher as compared to untreated clay or acid treated clay. This probably arises from its higher negative charge and the aggregation of the dye molecules on the surface.

The natural abundance and low cost of diatomite has drawn the attention of some researchers as a substitute for activated carbon. For example, the adsorption of basic blue 9 onto diatomaceous earth (diatomite) has been reported in the literature [85].The adsorption equilibrium revealed that diatomite can uptake 42 mmol dye/100 g in relatively low concentration in aqueous medium. The kinetics of adsorption of methylene blue onto the surface of diatomite at different operating condition was best described by the pseudo first order model. Diatomite has also been used for the removal of Sif Blau BRF (SB), Everzol Brill Red 3BS (EBR), and Int Yellow 5GF (IY) [86]. Values of the removal efficiency of the dyes ranged from 28.60 to 99.23%. The adsorption isotherms of SB, EBR, and IY were found to obey the Langmuir behavior, which indicates monolayer adsorption. It was suggested that the adsorbed dye anions form a monolayer with sulfonate groups as close as possible to the adsorbent surface [63]. In another study, the adsorption of three different dyes namely methylene blue(MB), reactive black (RB), and reactive yellow (RY) from aqueous solution by calcined and raw diatomite was reported [87,88]. It was noted that the percentage MB removal by calcined diatomite dropped from 33% to 2% with decreasing pH of dye solution from 12.0 to 2.0. The maximum removal occurred at basic pH (10–12). Furthermore, the removal rate decreased with the decrease in pH which may be due to excess H^+ ions competing with the dye cation for the adsorption sites. Also that, as the positive surface charge density decreases with an increase in the pH of the solution, the electrostatic repulsion between positively charged dye (MB^+) and the surface of the calcined diatomite was reduced resulting in more adsorption. The percentage removal of Reactive Yellow(RY) by calcined diatomite decreased with further increase in pH above pH 4 and the maximum percentage of removal was in acidic media (pH 2–3), while the percentage of Reactive Black (RB) removal was nearly constant over the pH range. In general, the percentage RB and RY removal was decreased from 24% to 14% and 22% to 1%, respectively with increasing pH of dye solution from 2.0 to 11.0 when calcined diatomite was used as the adsorption media. The percentage of MB, RB, and RY removal from solution remained constant by raw and calcined diatomite in the pH range from 4 to 10 with better removal by diatomite.

Sepiolite is a good adsorbent for organic species because it exhibits a variety of attractive properties such as high specific surface area, high porosity and surface activity. Because of their structural morphology, sepiolites have received considerable attention with regard to the adsorption of organics on the clay surfaces and to their use as support for catalysts [89]. The adsorption of Acid Red 57 on sepiolite has been reported in the literature [57]. In this case a practical limiting adsorption capacity was found to vary with pH and ionic strength of the solution. Maximum value of adsorbed dye was found to be 13.5 μmol/g of the adsorbent. This value is comparable with other studies on dye adsorption using low cost adsorbents [90,91]. The adsorption of diquat (DQ), paraquat (PQ) and methyl green (MG) on sepiolite has also been reported in the literature [92,93]. The largest amounts of DQ, PQ and MG adsorbed were between 100% and 140% of the cation exchange capacity (CEC) of sepiolite which translates to 0.75 moles of MG per Kg of the clay. There are also few reports in the literature regarding the use of modified sepiolite for adsorption of dyes. In one such report it was found that the adsorption of dye under investigation, namely Crystal Violet (CV) is highly affected by the sepiolite surface features[94]. The observed results showed that the amount of adsorbed CV cations on the base activated sepiolite is 2.6 fold higher than raw sepiolite. This was attributed to the fact that the basic activation leads to the replacement of part of Mg^{2+} ions located at the edges of the channels by Na^{+}, the reactivity of basal and edge surface groups is enhanced and consequently the adsorption capacity of base activated adsorbent is increased. On the other hand the low adsorption capacity on the Al-saturated samples of sepiolite arises from the aluminium cation exchange process which leads to pore blocking and the reactivity of basal or edge oxygen atoms of the silicate.

Natural zeolite is an abundant resource of aluminosilicate and has been explored as an effective adsorbent for pollutant removal. It has been shown that this material can be used to remove dyes from solution as well, for example the removal of Malachite Green(MG) was carried out on zeolite and the adsorption capacity was reported to be 5×10^{-5} mol/g [95]. This capacity was found to decrease in the presence of Pb^{2+} ions indicating the selective behavior of zeolite for smaller species. The adsorption behavior for Methylene Blue(MB) and Rhodamine B(RB) is also reported in the literature[96]. For methylene blue, the adsorption capacities were found to be $6.8\text{x}10^{-5}$ and $7.9\text{x}10^{-5}$ mol/g at 30 and 50 ◦C, respectively. In contrast, the adsorption capacities of rhodamine B were found to be $2.1\text{x}10^{-5}$ and $2.8\text{x}10^{-5}$ mol/g at 30 and 50 ◦C, respectively. Thermodynamic and kinetic calculations indicate that the adsorption was endothermic reaction with two-step diffusion process.

The adsorption of three reactive azo dyes (Reactive Black 5, Red 239 and Yellow 176) by two natural mezoporous minerals has also been examined in order to identify the ability of these minerals to remove coloured textile dyes from wastewaters [97]. For this purpose natural and modified sepiolites and zeolites were chosen. The adsorption results indicated that both natural sepiolite and zeolite have limited adsorption capacities of the reactive dyes but are substantially improved upon modifying their surfaces with quaternary amines. The maximum adsorption capacities for the three dyes namely Black, Red and Yellow on modified zeolite were found to be 111.1 g/kg, 88.5 g/kg and 60.5 g/kg respectively. The adsorption capacity decreased in the order of hydrophilicity of the dye molecule as: Red >

Yellow > Black. The adsorption of basic dyes (MG-400 and MS-300) from aqueous solutions onto natural zeolite is also reported in the literature and it was found that the adsorption capacities of MG-400 and MS-300 were 15 and 55 mg/g, respectively [98]. Natural zeolite and synthetic zeolite, MCM-22, have also been employed as effective adsorbents for a basic dye, methylene blue, removal from wastewater. It was found that MCM-22 exhibits equilibrium adsorption at $1.7\text{x}10^{-4}$ mol/ g as compared to the equilibrium adsorption value of $5\text{x}10^{-5}$ mol/ g obtained in the case of natural zeolite [99]. ZSM-5 and Beta zeolites, both in NH_4-form, were found to be the most efficient in enhancing total organic carbon (TOC) for printing ink removal from simulated wastewater water[100]. At concentrations of 5 g/L, the zeolites decreased TOC value by more than 50% from pretreated water by flocculation. In comparison with activated carbon of the same concentration, the zeolites were found to be 20% more effective.

Besides these common clays, there are numerous other examples available in the literature on the use of many other clay types such as halloysite, saponite, spent activated clay, palygorskite, hectorite, activated bleaching earth etc for the adsorption of dyes [101-106]. In some cases a mixture of clays has also been used by some researchers as potential adsorbents for dyes [107-110]. The results presented in all the studies above show that clay materials may be promising adsorbents for environmental and purification purposes.

CONCLUSION

The presence of organic pollutants in our environment has taken a serious turn in modern times. Their removal from soils and water bodies has drawn a great deal of attention from all quarters of scientific community. Various approaches have been put forwarded to remove these pollutants from aqueous media. The adsorption process because of its low cost and easy to handle approach has topped the list of all the methods employed in such work. The use of many adsorbents for such purpose requires that they should be easy to handle, readily available or cheap to produce, environmentally compatible and give good results at the end. Clays of various types have drawn a great deal of attention in this regard and a substantial number of studies in the literature have revealed their usefulness as a potential means of removing pollutants especially dyes from aqueous media. However there is yet little information available in the literature containing a full study of comparison between types of adsorbent clays.

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Chapter 12

THE BEAUTY OF COLORS: THE YELLOW FLAVONOLS IN SCIENCE AND ART

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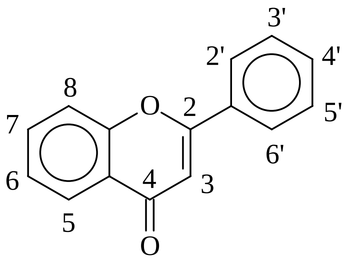
ABSTRACT

Dyes extracted from plants have been used for centuries for coloring materials. In this paper, typical behaviors of some naturally occurring colorants belonging to the class of flavonoids are presented. Their structures derive from that of flavone (2-phenylbenzopyrone), which is colorless, whereas hydroxy derivatives absorb UV and blue light, so appearing yellow colored. Current interest in flavonoids is mainly due to their varied biological activity in medicine, but also to their use as colored components in works of art (tapestries, carpets, miniatures).

The color of hydroxy-substituted flavonoids (flavonols) can be markedly modified by changing the pH or bonding with different metal ions, therefore, it critically depends on the acidity and the presence of metals in the environment. The absorption and emission spectra generally shift to the red by increasing the pH, due to stabilization of anionic forms. The number and sequence of acid-base dissociation steps depend on the number and position of the hydroxy-substituents. These aspects will be illustrated here with some significant examples concerning two naturally occurring colorants, old fustic and weld, and their main chemical components (morin, apigenin and luteolin). Absorption and fluorescence spectra recorded in solution provide the base for developing scientific investigations on the colorants spread on paper as watercolors or used in mordant dyeing of textiles.



Scheme 1.

INTRODUCTION

Since from prehistoric times, human kind have been fascinated by the beauty of colors and used in their artefacts those offered by nature, isolating colorants from minerals, plants and animals. It was only during the nineteenth century that synthetic colorants became available and today synthetic dyes and pigments are industrially produced and make more pleasant our everyday lives in coloring textiles, vehicles, toys and even foods. The sensitivity of the human eye to colors increases from red to yellow and then declines from yellow to violet. So yellow is highly visible and is perceived as the brightest color. Used in the past for signaling sickness on board ship and currently to highlight toxic or radioactive hazards, yellow has been sometimes considered as an unpleasant color, but looking at an expanse of sunflowers or even its representation by outstanding painters, we perceive it as a beautiful color in nature and art.

In this article, our interest is focused on naturally occurring colorants used in works of artistic or historical importance and in particular on some yellow colorants belonging to the class of flavonoids. In nature, these compounds, which are responsible for white, yellow and orange colors of a wide variety of flowers and fruits, occur mainly as glycosides (sugar derivatives). Their structures derive from that of flavone, the 2-phenylbenzopyrone (Scheme 1), which is colorless, whereas its poly-hydroxy derivatives (flavonols) absorb UV and blue light, so appearing yellow colored. An overview on naturally occurring flavones and flavonols has been recently published. [1]

Due to very strong absorption of UV-B light, they may play a role in preventing damage to leaves by ultraviolet radiation as also have insecticidal or insect-repellent properties. [2] This means that plants use flavonoids as defense and signaling compounds. Their beneficial effects are also felt by human kind: characterized as antioxidants, they offer protection against a number of degenerative diseases. Current interest in flavonoids is therefore mainly due to varied biological activity because of their antioxidant, antiradical and anti-inflammatory properties. [3-5] Moreover, they are also stimulating scientific interest in the field of the knowledge, restoration and conservation of works of art where they have been mainly used, such as tapestries, carpets, miniatures, or only used for glazing or final touches, as in paintings with different techniques. When used in painting, dyes are transformed into lakes, [6] which have constituted artists’ palette and have been widely used from the Middle Age until the early nineteenth century. Lakes, to be applied on dry surfaces, are previously mixed with a binder (gum Arabic, egg, casein, oil) which allows the pigment to adhere to the support. When these colorants are used for dyeing textiles, a mordant is generally needed. The mordant plays multiple functions: ensures brightness and fastness of the dye and also has influence on the final color obtained. Because of the chromatic changes they undergo interplaying with various metal ions, [7,8] flavonoids behave like ionochromic compounds. Chelating the transition metals also causes their potentiality to inhibit hydroxy radicals. [9]

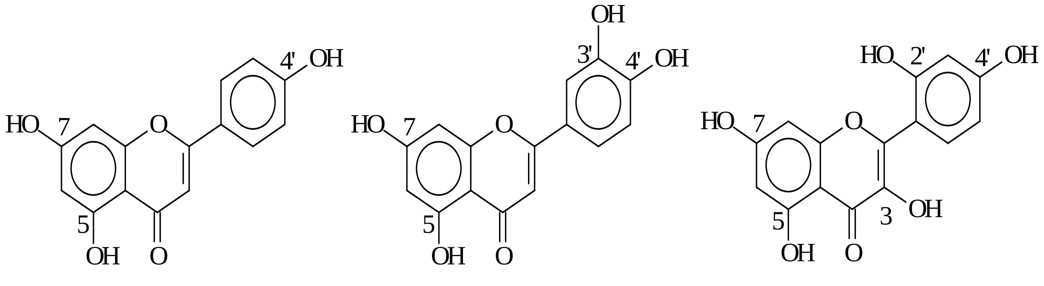
The color of flavonoids can also be markedly modified by changing the pH, [7,10] therefore, critically depends on the acidity of the environment. Thus, they are also acidichromic compounds. The effect of increasing the pH generally results in shifting the absorption and emission spectra of flavonoids to the red. Since artifacts are subject to atmospheric pollutants, they can undergo significant chromatic changes when the environment changes. During the last decades, acidic rains have been one of the most important causes of pollution and may have attacked painted artifacts. One of the reasons to study the effect of pH on the absorption and fluorescence spectra of colorants is to obtain information about the degradation processes in artistic works and to understand which was their original appearance. A further cause of degradation of organic dyes is exposure to light (photoageing) which generally results in bleaching and/or changes of color. [11]

These aspects will be illustrated here through some significant examples concerning the main chemical components of the naturally occurring colorants, fustic and weld. The most common yellow dyes were extracted from weld (*Reseda luteola* L.), young fustic (*Cotinus coggyria* Scop.), old fustic (*Chlorophora tinctoria* L. Gaud.), which came from the West Indies, and berries from *Rhamnus*. [12-14]

The chemical components here investigated are apigenin (5,7,4’-trihydroxyflavone, AP) and luteolin (5,7,3’,4’-tetrahydroxyflavone, LU), both from weld, and morin (3,5,7,2’,4’-penta hydroxyflavone, MO), from old fustic (Scheme 2):

It will be shown, starting from the less substituted molecule (AP), how the presence of additional hydroxyl groups and their position can alter the photophysical behavior in the flavone structure.

AP, which is present in small percentages in weld, is contained in many fruits and vegetables (parsley, onions, orange, tea, wheat sprouts, chamomile, etc). Being non-toxic and non-mutagenic, it is considered an important component in food and also a drug with high therapeutic potentials. [15]



apigenin (AP) luteolin (LU) morin (MO)

Scheme 2.

LU is the main component of weld, which has been used since Roman times as an orange pigment, and until recently for dyeing silk. The mordant most frequently adopted to fix and stabilize the color on the fibre, has been alum, but other salts are also used to obtain different shades. With alum mordant, weld produces a yellow-orange color on wool and silk, with copper it generates a greenish yellow color, with iron it becomes olive. [12,16]

MO is the coloring principle of old fustic, [17] the wood of Morus tinctoria, a tree of Central America which is used principally for dyeing wool. Changing mordant, the color changes: with chromium it gives an olive green, with aluminum and tin, it is yellow, and with iron, morin becomes a deep olive brown.

METHODOLOGIES AND TECHNIQUES

To investigate organic coloring materials in works of art, several analytical techniques have been applied that were mainly aimed at identifying colorants, understanding their degradation processes and preventing further damages. The main difficulties in this study arise because coloring materials are often present in small quantities, mixed with other compounds and altered by ageing which results in molecular degradation and fading of the original colors. In addition, most techniques require samples to be removed for analysis. Generally, samples are very small in size, usually prepared as thin or cross-sections to be investigated by microscopic techniques, or to be transformed into solutions to be analyzed by some micro-destructive technique. So, there is a great need for analytical means that could perform molecular identification of very small amounts of dyes, present in complex mixtures of aged materials. Moreover, a non-destructive approach is highly desirable, especially for investigating significant operas of historical or artistic importance, and in particular when sampling is absolutely forbidden, as it happens for miniatures. Recent technological developments have made available improved diagnostic techniques and especially easily portable instrumentation for *in situ* non-destructive investigations on original artifacts.

So far, the most widely used techniques have been chromatography and spectroscopy.

For several years, chromatography has been widely applied for the identification of dyes on works of art, [18] mostly using UV– Vis spectrophotometry and mass spectrometry for detection. For example, very recently, high pressure liquid chromatography with mass spectrometric detection (HPLC-MS) has allowed the different components, which are present in the extracts from textiles, to be analyzed [19-23] as well as to investigate color fading on textiles [24] and recognize natural dyes and their degradation products in archeological objects. [25]

At the same time, considerable attention has bee paid and efforts have been invested in extending the applications of spectroscopic techniques as methods for identifying materials used in paint. Absorption spectrophotometry has been proposed for identifying organic colorants [26] and fluorimetric techniques have been experienced to characterize both pigments and binders. [27-31]

Information that can be obtained from spectroscopic studies concerns several molecular properties that can be useful in diagnostic of colorants as well as to understand the complex mechanisms of their interactions with supporting materials and of ageing processes. From steady state UV-Visible absorption and fluorescence spectroscopy, wavelength range and intensity measurements provide information about the electronic excitation energy and the nature of the excited state. From time-resolved techniques, additional information is obtained concerning the different and competing relaxation pathways of the electronically excited state.

Up to date, steady state spectroscopic techniques have been developed in portable version and applied to in situ measurements. [32] Only very recently, an instrument for time resolved fluorescence measurements was realized and tested in portable format. [33]

In situ character of spectroscopic techniques vs immovability of chromatographic techniques makes the former more easily handled in the study of artifacts. Nevertheless, due to the complementary information that they give, application of both is desirable and fruitful, as shown from recent works where these techniques were both applied in the same context. [34,35] Furthermore, modern conservative protocols strongly suggest to perform preliminary non-destructive measurements in order to minimize and guide the sampling procedures for micro-destructive analysis.

EFFECT OF pH ON UV-VISIBLE ABSORPTION AND FLUORESCENCE SPECTRA

The electronic absorption spectrum of flavonols is characterized by two principal bands, that can be related to the moieties constituting their skeleton. Theoretical calculations on the electronic transitions of 2- phenylchromones have been carried out considering that the absorption spectrum is formed by transitions localized on ortho-hydroxybenzaldehyde, chromone and the phenyl fragment. [36] The long-wave transition is mainly localized on the benzaldehyde fragment. The shorter wavelength transitions involve phenyl chromone and benzaldehyde moieties and have a pronounced charge transfer character (Figure 1). [36]

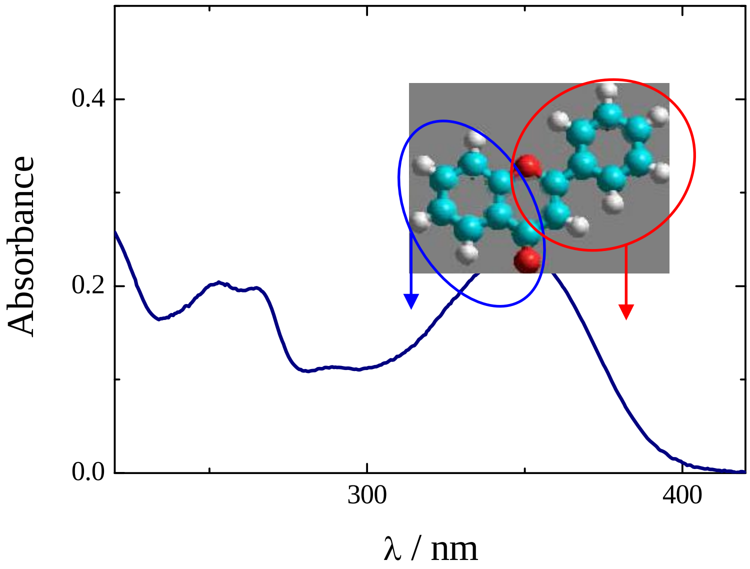


Figure 1. Typical absorption spectrum of flavones and band assignments.

The unsubstituted flavone (Scheme 1) is colorless since both absorption bands are located in the UV spectral region (λ_{max} = 250 and 294 nm).

When hydroxyl groups are introduced into the chromone fragment of flavone, they cause changes mainly in the transitions localized on that fragment, affecting the energy of benzaldehyde- and chromone-type transitions. For 5-hydroxy-, 7-hydroxy- and 5,7-dihydroxy-phenylchromones, the lower energy transition is expected to shift towards longer wavelengths, [36] thereby producing color.

When hydroxyl groups are introduced into the phenyl fragment an energy decrease and an increase in the oscillator strength should occur for the phenyl-localized transitions.

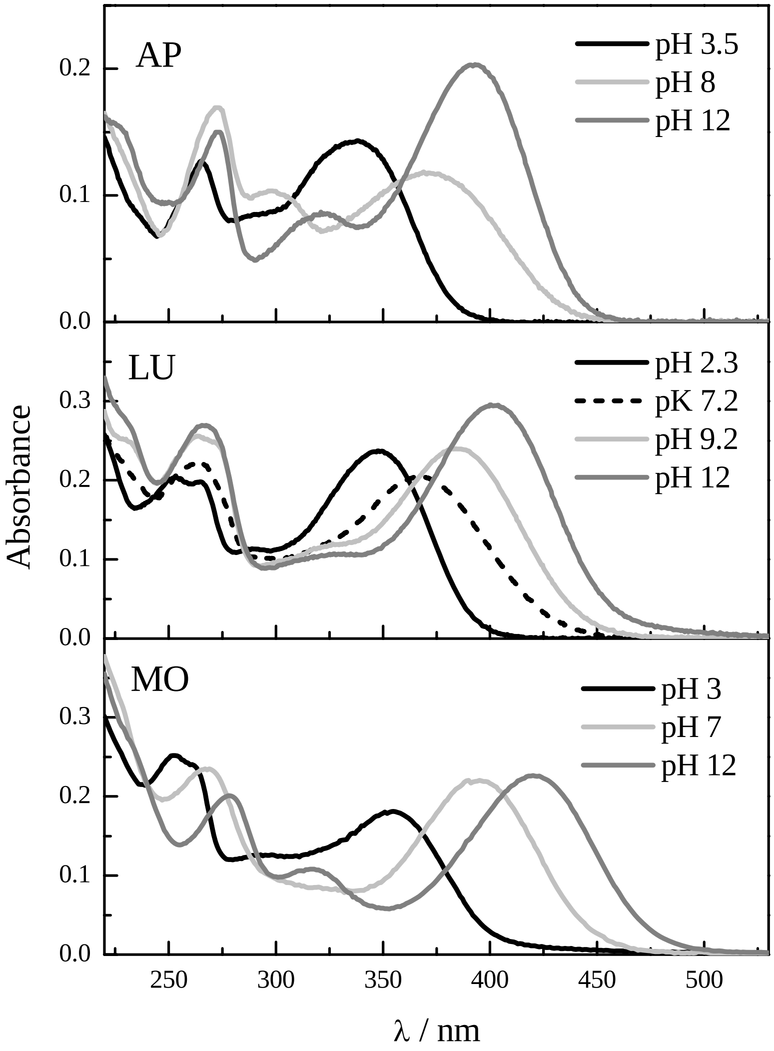


Figure 2. Absorption spectra of the three flavonols in water/methanol 2:1 (v/v) solution at different pH values.

Table 1. pK values and maximum absorption wavelengths (λ_{max}) of flavonols in water/methanol 2/1 v/v

	AP	LU	MO
λ_{max} / nm (neutal form)	265, 337	253, 348	253, 355
pK_1	6.6	6.9	4.6
λ_{max} / nm (monoanion)	372	366	395
pK_2	9.31	8.6	10.3
λ_{max} / nm (dianion)	392	384	421
pK_3		10.3	
λ_{max} / nm (trianion)		401	

The spectral behavior of the compounds here presented is in substantial agreement with expectation. When hydroxyl groups are introduced in the 2-phenylbenzopyrone skeleton to yield the flavonol structures (Scheme 2), the higher energy band is scarcely influenced, whereas the lower energy absorption shifts to the red and the solutions become pale yellow. The bathochromic shift increases with the number of hydroxyl groups, as can be seen in Table 1 (λ_{max} values, first line) on going from AP to LU and to MO.

The spectrum also changes by changing the pH: a pH increase causes the color of the solutions to turn from pale yellow to intense yellow-orange, due to a further bathochromic shift of the absorption spectrum. The absorption spectra of AP, LU and MO at different pH values in water/methanol 2:1 (v/v) solution are shown in Figure 2.

The study of the pH effect on the absorption spectra of AP, LU and MO allows the pKs of these molecules to be determined and the absorption spectra of the neutral, mono-anionic and di-anionic ground state species to be assigned (Table 1 and Figure 2).

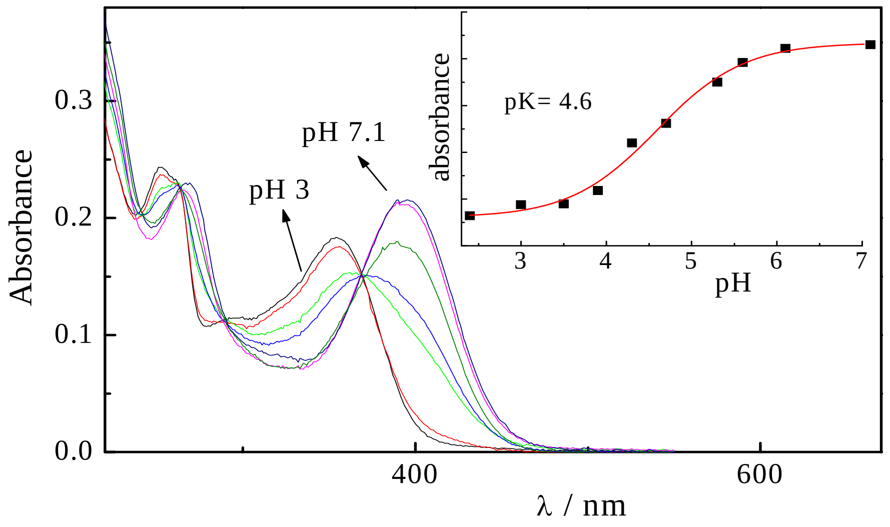


Figure 3. Evolution of the absorption spectrum of MO observed upon increasing the pH. Inset: spectrophotometric titration (λ_{anal} = 395 nm).

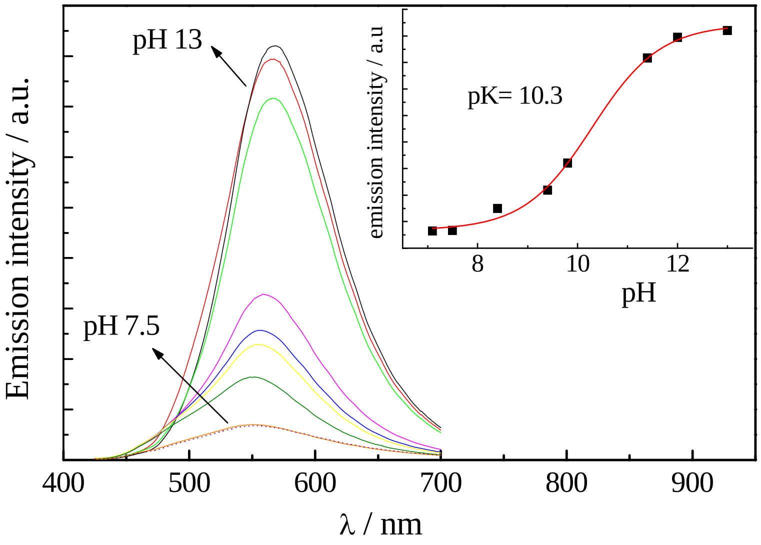


Figure 4. Evolution of the fluorescence spectrum of MO observed upon increasing the pH. Inset: fluorimetric titration (λ_{exc} = 397 nm, λ_{anal} = 560 nm).

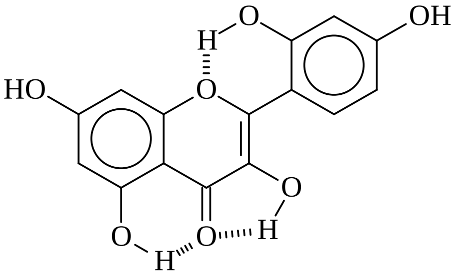
The pKs can be determined by both spectrophotometric and fluorometric titrations; when the values obtained match, as for the compounds under investigation, the excited state relaxes before acid-base equilibration is established in the excited state. The number and sequence of acid-base dissociation steps depend on the number and position of the hydroxyl groups. Examples of spectral evolution upon increasing the pH and of both kinds of titration are shown in Figures 3 and 4 for absorption and fluorescence, respectively.

In the case of LU, three deprotonation steps are detected (pK = 6.9; 8.6; 10.3), [7] only two for AP (pK = 6.6; 9.3) [7] and MO (pK = 4.6; 10.3), see Table 1. Other literature results for LU [37] are substantially in agreement with those here presented, whereas for MO, an intermediate value (8.37) has been also reported. [38] Since pK_1 values are substantially the same for LU and AP, we believe [7] that in both these molecules the first ionization involves the OH group in 7 position, which is the most acidic one due to the inductive electron-attracting effect of the 5-OH, stabilized by H-bonding to the carbonyl. In the mono-anions, the negative charge (O^- in 7 position) decreases the intrinsic acidity of the other OH groups in the molecule. Since the spatial distance between the two negative charges should be as large as possible to stabilize the di-anionic species, the second deprotonation probably occurs at the 4’-OH group in the 2-phenyl moiety. Its acidity is higher for LU than for AP (pK_2 lower for LU than for AP) because the inductive electron-attracting effect of the 3’-OH group on the nearby 4’-OH group increases its acidity.

The situation changes with MO, for which the neutral form results to be notably more acidic than those of AP and LU. The most relevant differences with respect to the other molecules are hydroxy-substitutions in the 3 and 2’ positions. The 4-carbonyl can give intramolecular hydrogen bond with both the 5 and 3 hydroxyls. However, the bond with the 3-OH, yielding a pentatomic ring, is weaker than the one with the 5-OH that forms a six membered ring, which is sterically and energetically more favored. [39]. Moreover, the 2’-OH can be hydrogen-bonded to the ring oxygen, leading to a quasi-planar structure (Scheme 3), thus increasing the conjugation and therefore also the acidity.

This is what is experimentally observed. In accordance with others, [40] the first proton dissociation should occur at the 3-hydroxy group, whose greater acidity than any other hydroxyl group of MO is due to its close proximity to the electronegative 4-keto oxygen.

The fluorescence emission of flavonols (Table 2) is more or less intense depending on the structure and the degree of deprotonation. For LU, the emission cannot be detected for the neutral form whereas it is observed in the anionic forms. For AP, the fluorescence intensity, which is very weak in neutral solution (emission quantum yield, $\Phi_F \sim 4 \times 10^{-4}$), increases with increasing the pH and the emission maximum shifts to the red.



Scheme 3.

Table 2. pH effect on the fluorescence properties of the flavonols investigated and their anions in water/methanol 2/1 v/v

	AP	LU	MO
λ_{max} / nm (neutral form)	440	not observed	524
λ_{max} / nm (mono-anion)	470	518	545
λ_{max} / nm (di-anion)	470/570	522	565
λ_{max} / nm (tri-anion)		518	

Table 3. Photophysical parameters of MO in ethanol and ethanol/water solution (1/2 v/v): maximum wavelength (λ_{max}), Stoke-shift ($\Delta\nu$), fluorescence quantum yield (Φ_F), fluorescence lifetime (τ_F), relative amplitudes of the two fluorescence components (A %), radiative (k_F) and non-radiative (k_{NR}) relaxation kinetic constants

Solvent *(prevalent species)*	λ_{max} (nm)	$\Delta\nu$ (cm^{-1})	Φ_F	τ_F ($\times 10^{-9}$ s)	A %	k_F ($\times 10^{8}$ s^{-1})	k_{NR} ($\times 10^{9}$ s^{-1})
methanol	554	7330	0.046	2.63 0.41	9% 91%	1.1	2.3
pH 2.6 *(neutral)*	524	9085	0.014	2.33 0.07	12% 88%	2.0	14
pH 7.5 *(mono-anionic)*	545	7032	0.039	2.57 0.20	59% 41%	0.15	0.4
pH 13 *(di-anionic)*	565	6110	0.097	1.59 0.57	21% 79%	1.7	1.6

The most intense fluorescence is exhibited by MO ($\Phi_F = 1.4 \times 10^{-2}$, in neutral form), for which the results of a detailed photophysical study as a function of the pH are reported in Table 3.

It can be observed that two decay components are present with different contributions. The radiative (k_F) and non-radiative (k_{NR}) relaxation kinetic constants are calculated from the relationships:

$$k_F = \frac{\Phi_F}{\tau_F}$$

and

$$k_{NR} = \frac{1}{\tau_F} - k_F$$

taking into account only the principal component, thus the data obtained have to be considered merely indicative. The relative positions of the absorption and fluorescence spectra of MO at different pH are illustrated in Figure 5, from where the large Stoke-shifts are evident (see Table 3).

In order to interpret the peculiar behavior of MO - that is, the marked spectral Stoke-shift and the acidity higher than for the other two dyes - a comparison with the simpler parent molecule, the 3-hydroxyflavone, 3-HF (Scheme 4), can be useful.

The 3-HF has been object of notable interest as a model molecule suitable for studying intramolecular proton transfer in the excited state (ESPT). [41-44] Interaction of the 3-OH with the adjacent 4-carbonyl brings to a resonance stabilized tautomer (Scheme 5).

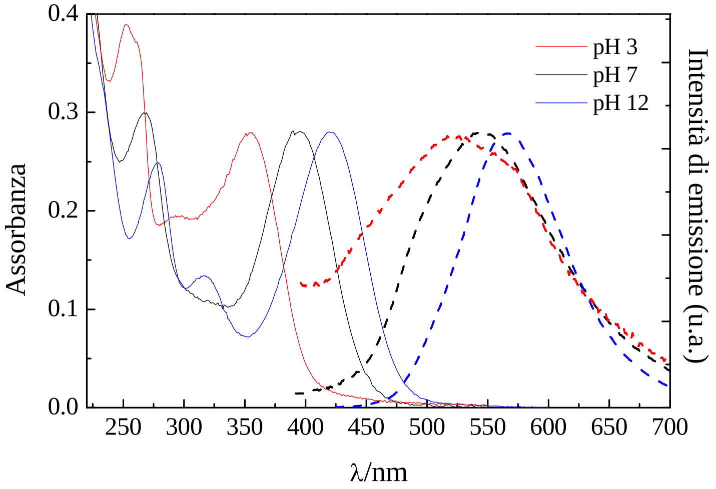
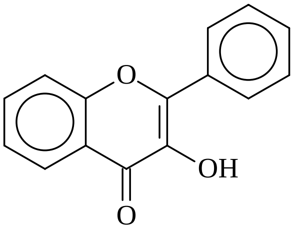
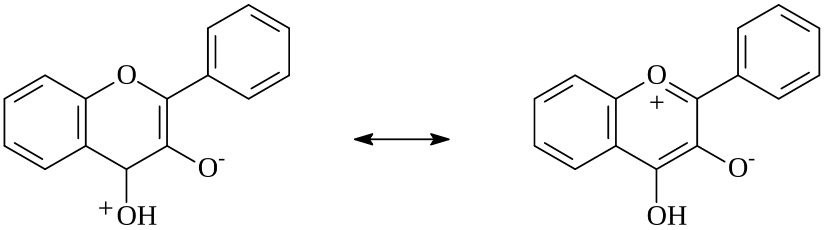


Figure 5. Normalized absorption and emission spectra of MO in MeOH-water (1/2 v/v) solution at different pH values.



Scheme 4.



Scheme 5.

In the ground state, the 4-keto form (Scheme 4) represents the molecular structure at the best, whereas proton transfer leading to the tautomer is favored in the excited state. For this compound emission bands were found at 406 and 531 nm in methanol. [45] The system has been represented by double-minimum potential energy surfaces. [46] In the ground state, the lowest minimum corresponds to the 3-hydroxy-4-keto form, whilst, in the excited state, the lowest energy corresponds to the tautomer. Therefore, the molecule absorbs in the 3-hydroxy-4-keto form but can fluoresce from the tautomeric form, being the tautomerization barrier very low in the excited state (Figure 6).

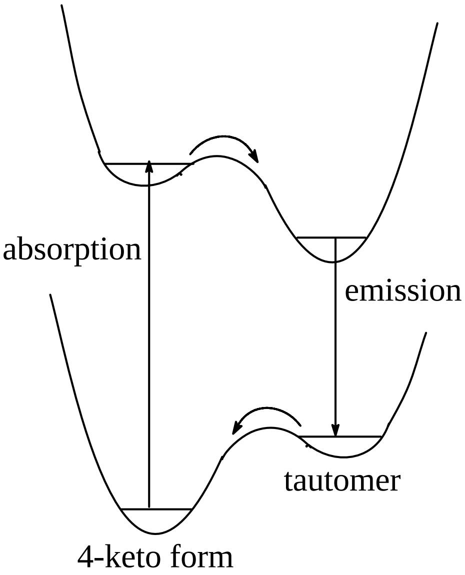


Figure 6. Model for ESPT.

This model explains the unexpected finding that a compound absorbing in the blue-violet, such as MO, exhibits a yellow-green emission, which arises from the tautomer.

EFFECT OF METAL IONS ON UV-VISIBLE ABSORPTION AND FLUORESCENCE SPECTRA

Flavonols exhibit a great propensity towards complex formation with metal ions. Metal ions are used in dyeing textiles as mordants to fix and stabilize the color on the fibre. Thereby, the interactions with metal ions significantly influence the color and fastness of the dye. [9] The ionochromism of flavonols will be here illustrated with some meaningful examples by analyzing the changes in spectral properties due to increasing additions of Al^{3+} and Ca^{2+} ions to their methanol solutions. Multi-step interactions are generally observed.

The occurrence of two consecutive reaction steps following additions of Al^{3+} to an AP methanol solution is illustrated in Figure 7.

In the first step (Figure 7 a), a new band grows at 382 nm, with maintenance of isosbestic points up to $[Al^{3+}]$~ 8×10^{-5} mol dm^{-3}, which indicates a clean reaction. Further additions of Al^{+3} (from 10^{-4} to 10^{-3} mol dm^{-3}) induce spectral changes in the UV region, without significantly affecting the color band (Figure 7 b), which suggests that a subsequent interaction with the metal ion occurs. The spectral position of the bathochromic absorption is close to that reported for the complex of 5-hydroxyflavone (397 nm). [47,48] The association with Al^{3+} significantly enhances the fluorescence intensity of the dye, originating an emission band at 525 nm, with a large Stokes' shift (~ 7100 cm^{-1}). The fluorescence excitation spectrum is quite similar to the absorption one. The emission quantum yield, $\Phi_F = 1.2\times10^{-2}$ (with $[Al^{3+}] = 10^{-3}$ mol dm^{-3}), is almost two orders of magnitude larger than that of pure AP ($\Phi_F = 4\times10^{-4}$).

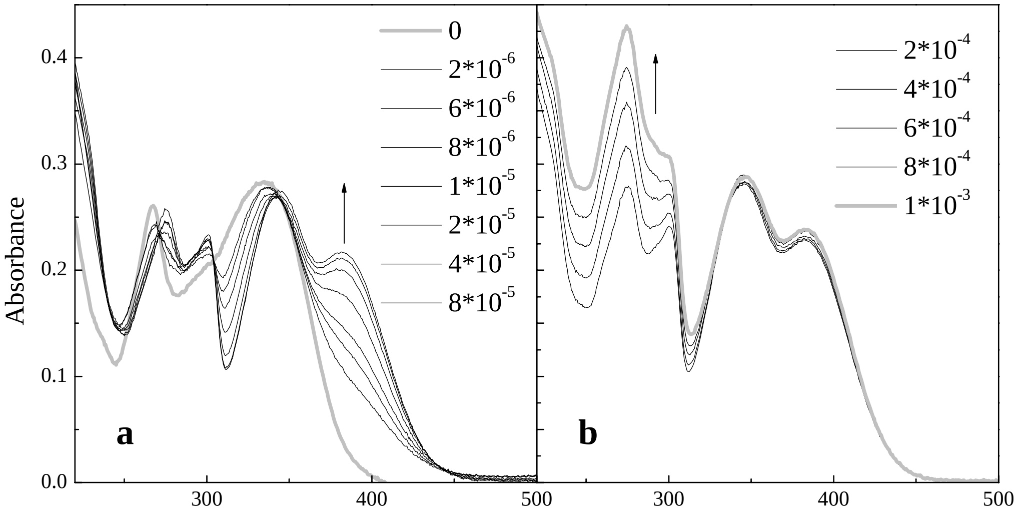


Figure 7. Effect on the absorption spectrum of the addition of Al^{3+} ions to a methanol solution of AP (1.14×10^{-5} mol dm^{-3}). a: $[Al^{3+}]$ 0 - 8×10^{-5} mol dm^{-3}; b: $[Al^{3+}]$ 2×10^{-4} - 1×10^{-3} mol dm^{-3}.

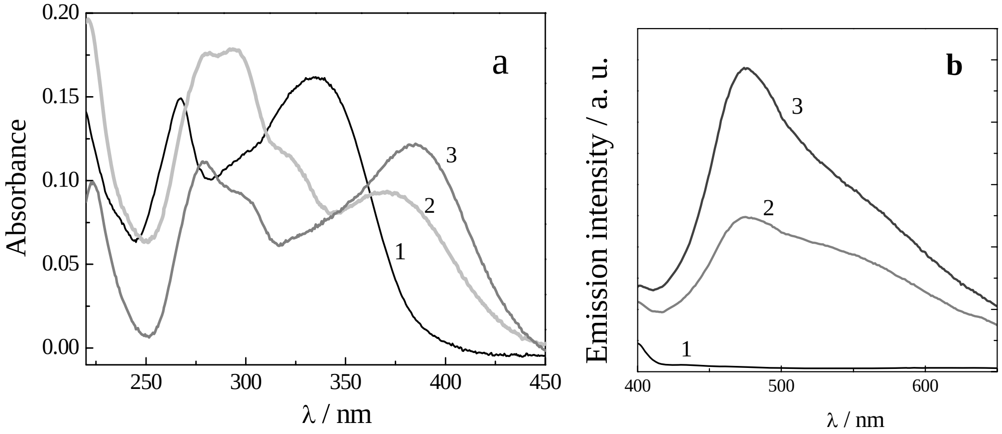


Figure 8. Absorption (a) and emission (b) spectra of a 8×10^{-6} mol dm^{-3} AP methanol solution. *1:* [Ca^{2+}] = 0; *2:* [Ca^{2+}] = 0.2 and *3:* [Ca^{2+}] = 0.5 mol dm^{-3}.

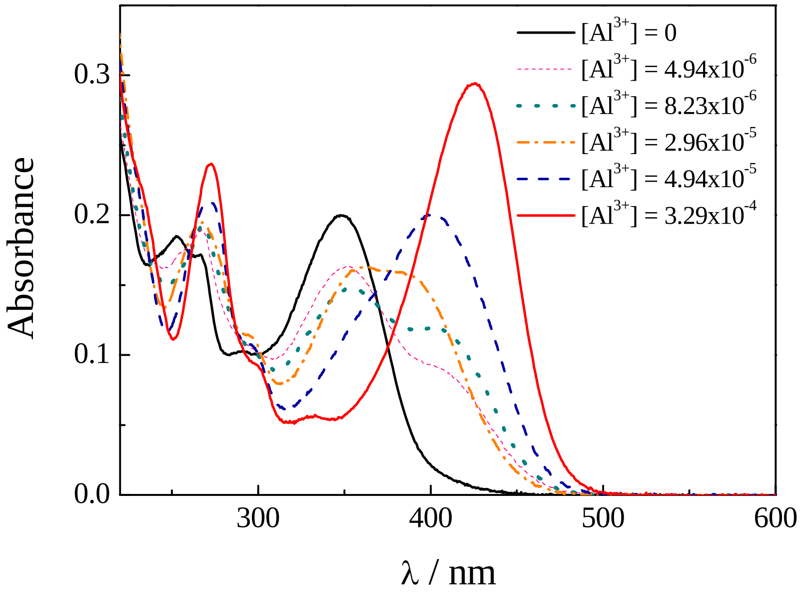


Figure 9. Effect of the addition of Al^{3+} ions ([Al^{3+}] : 0 – 3× 10^{-4} mol dm^{-3}) on the absorption spectrum of a methanol solution of LU (2.7× 10^{-5} mol dm^{-3}).

This dye is less prone to give complexes with calcium than with aluminium, since the spectrum starts to change only when the concentration of Ca^{2+} is approximately 10^3 times larger than that of AP. This could explain the fact that weld lakes containing calcium salts are less stable than those on hydrated alumina [49]. The absorption spectra of AP/Ca^{2+} methanol solutions at different Ca^{2+} concentrations (spectra 2 and 3) are compared in Figure 8a with those of free AP (spectrum 1).

Isosbestic points are not maintained, even for restricted concentration ranges of Ca^{2+} additions. This denotes that complex formation occurs in overlapped steps. Here again, the fluorescence of the complex (Figure 8b) is markedly enhanced ($\Phi_F = 1.4\times10^{-2}$, at [$Ca^{2+}$] = 0.5

mol dm^{-3}), compared with that of the free dye, and shows a maximum at 474 nm and a broad shoulder around 540 nm. The fluorescence maxima and intensities vary with the amount of added ions, further supporting the hypothesis that different molecular complexes are formed. Some similarities are observed between the spectra of the complexes and those of the deprotonated species.

Also LU exhibits a great affinity with metal ions. The overall spectral changes observed by adding Al^{3+} ions to a methanol solution of LU are shown in Figure 9. As can be argued from the spectra, multiple interactions occur, leading to an overall bathochromic shift of the color band; even in the UV region marked variations are observed.

The individual steps are tentatively separated in Figure 10 a and b. The first interaction occurs in the 10^{-6} – 10^{-5} mol dm^{-3} Al^{3+} concentration range; new bands appear at 267 and 402 nm and isosbestic points are maintained (Figure 10a).

In the 8×10^{-6} – 3×10^{-5} mol dm^{-3} [Al^{3+}] range (Figure 10b), where the dye and the ion are present in comparable amounts, no isosbestic point is maintained and the global spectral pattern slightly shifts back to the blue. A regular spectral variation towards the red starts again when [Al^{3+}] ~ 5×10^{-4} mol dm^{-3}. The final limit spectrum ([Al^{3+}] $\geq 10^{-4}$ mol dm^{-3}) shows a bathochromically shifted, very intense band at 425 nm. Absorbances at selected wavelengths, corresponding to the most significant spectral variations, that are plotted as a function of the total Al^{3+} added (logarithmic scale) in Figure 11, illustrate the multiple-step complexations.

Additions of Al^{3+} ions induce fluorescence emission in the non-fluorescent methanol solutions of LU, with a maximum initially located at 570 nm (from [Al^{3+}] = 10^{-6} to 10^{-5} mol dm^{-3}), which shifts to the blue (540 nm at [Al^{3+}] ~ 3×10^{-5} mol dm^{-3}) and newly to the red (553 nm) upon further Al^{3+} additions (Figure 12). This trend parallels that of the absorption. The emission quantum yield is exceptionally high (Φ_F ~ 1). Therefore, fluorescence is the unique relaxation path of the excited state and this explains the high lightfastness of the chelate [8].

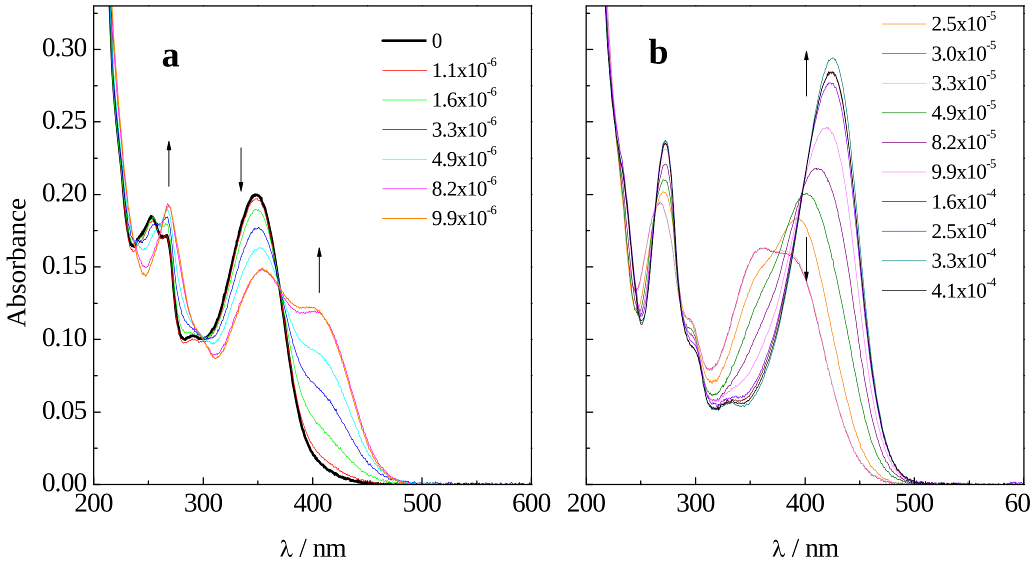


Figure 10. Evolution of the absorption spectrum of LU (2.7×10^{-5} mol dm^{-3}) upon addition of Al^{3+} ions. *a:* [Al^{3+}] = 0 – 10^{-5} mol dm^{-3}; *b:* [Al^{3+}] = 2.5×10^{-5} – 4.1×10^{-4} mol dm^{-3}.

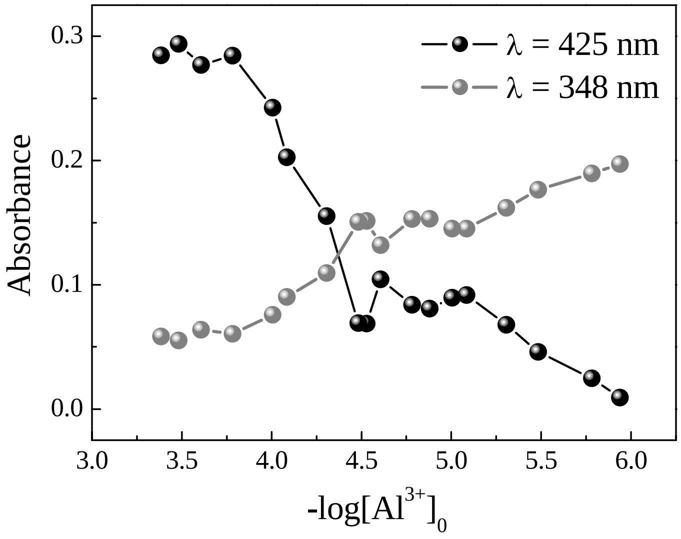


Figure 11. Absorbances of LU solutions (2.7×10^{-5} mol dm^{-3}) at two selected wavelengths as a function of *-log[Al^{3+}]*.

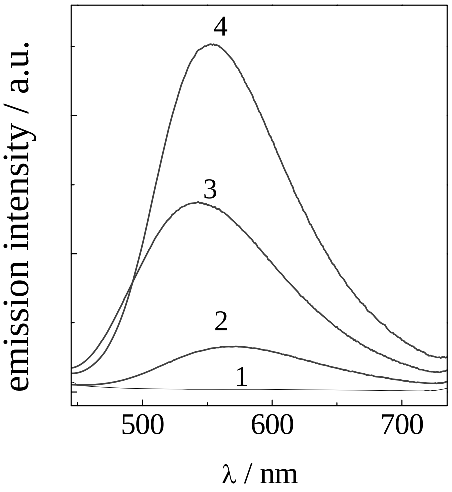


Figure 12. Emission spectra of the LU-Al^{3+} adducts at increasing concentrations of Al^{3+} ions. *1:* [Al^{3+}] = 0; *2:* [Al^{3+}] = 5×10^{-6}; *3:* [Al^{3+}] = 2.5×10^{-5} and **4**: [Al^{3+}] = 4×10^{-4} mol dm^{-3}.

Similarly, also MO interplays with various metal ions. With Al^{3+}, the absorption color band has been reported to shift to 420 nm and the corresponding fluorescence peak at 500 nm [50], a spectral evolution that parallels that due to deprotonation. Later, other authors [40] found that Aluminum and morin form complexes of 1:1 and 1:2 and/or 1:3 (Al/MO) stoichiometry, but at low total MO concentrations only 1:1 species were prevalent, exhibiting an absorption maximum at 420 nm and an intense fluorescence emission (not observed by the authors in the absence of metal [40]) at 510 nm. Even for MO, the affinity towards Al^{3+} ions is larger than that towards Ca^{2+} ions. [40]

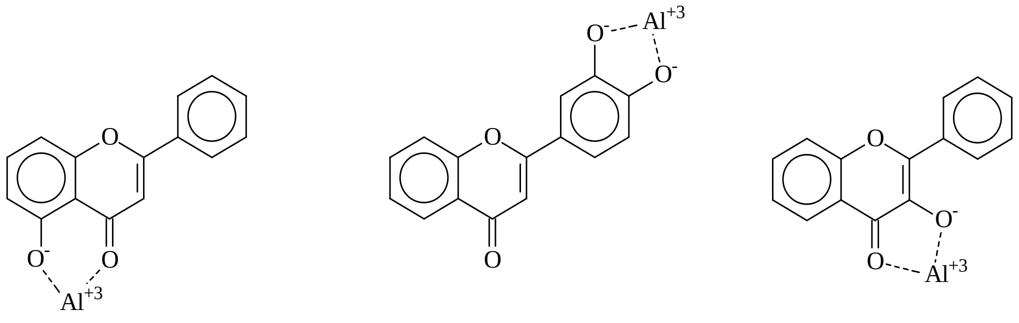
The spectral behavior of flavonols in the presence of Al^{3+} ions indicates their potential as chromogenic and fluorogenic sensors for cations. It has been reported that the fluorescence of the chelate of flavonols provides detection limits for Al^{3+} as low as a few parts-per-billion. [51] In the living organisms flavonoids, by chelating metal ions, may prevent metal-mediated generation of free radicals and, therefore, protect biological targets from oxidative stress. [52]

Despite the widespread use and diffusion of the metal-flavonols chelation reactions, debate continues regarding the stoichiometry of complexes formed in solution. Some authors claim that a free 5- and/or 3-hydroxy group are necessary for complex formation with metal binding that involves the hydroxy groups and the 4-keto group. [51] However, it has been recently demonstrated by UV-visible and Raman spectroscopies, combined with quantum chemical calculations, [53] that 3’,4’-hydroxyflavone in methanol undergoes chelation with Al^{3+} ions, forming a 1:1 complex (λ_{max} = 384 nm) by linking the only two hydroxyls present in the molecule.

Therefore, in the molecules here considered, there are three possible chelation sites (Scheme 6): the 5-hydroxy-4-keto assemblage (a), that all of them possess; the reciprocally ortho 3’,4’-hydroxyls (b), present in LU; and the 3-hydroxy-4-keto binding site (c), which is included in the MO structure:

Thus AP would be expected to exhibit the simplest behavior. However, even in this case, the spectral features can not be justified by an unique complex. It can be thought that the primarily formed complex is a 1:2 (Al^{3+}/AP) stoichiometry complex, that dissociates to a complex of lower stoichiometry (1:1) in order to further react with excess metal ions. However, a 1:1 initial complex of (a) structure, followed by interaction of Al^{3+} with the 4’-OH cannot be *a priori* excluded.

In the case of LU, the experimental results show the occurrence of at least three reaction steps in the complexation, that possibly involve both the 5-hydroxy-4-keto and the 3’,4’-hydroxyls binding sites. Here the existence of chelate of different stoichiometry, that is, 1:1, 1:2 and 1:3 (Al^{3+}/LU) can be reasonably proposed, their relative amounts changing with the Al^{3+} added. Even for LU the inversion of the trend in the spectral changes upon increasing Al^{3+} concentration induces to suppose that one chelate dissociates to form the other.



(a) (b) (c)

Scheme 6.

In the case of MO, where three different stoichiometry were foreseen for the chelates, [40] we can refer to the behavior of the model molecule 3-HF. For this compound a 1:2 (Al^{3+}/MO) stoichiometry complex is formed in methanol. [54] In the complex the normal fluorescence shifts to the red from 406 to 450 nm whereas that of the tautomer disappears, accompanied by an increase of quantum yield of almost two orders of magnitude [45]. It can be thought that for MO the 3-hydroxy-4-keto is the most easily attackable binding site, in accord with its weaker intramolecular hydrogen bond. The spectral findings support this hypothesis.

CONCLUSION

Despite the small structural differences among the three molecules here considered, their spectral properties are well distinguished, even in the absence of additives, as shown by the absorption and fluorescence spectra that shift to the red with increasing the number of the hydroxyl groups.

They behave as acidichromic and ionochromic molecules since in aqueous solution their color changes as the pH changes and in methanol solution their color changes upon metal ion additions.

The absorption and emission maxima move to the red and the fluorescence intensity increases on increasing the pH. Deprotonation increases conjugation, thus producing the bathochromic effect, and enhances the emission, probably because of the greater compactness of the ion where the contribution to deactivation of the excited state through OH vibrations is lost.

Chelation has an effect parallel to deprotonation. It shifts the absorption spectrum to the red, induces fairly intense fluorescence emission in LU ($\Phi_F \sim 1$) and significantly enhances the intensity of AP and MO fluorescence (by almost 100 times). The appearance (or enhancement) of emission when chelation occurs can be attributed to the lack of excited state vibrational relaxation through hydrogen bonding with the solvent, similarly to what happens for the deprotonated forms. The intense fluorescence induced by metal ions can be used as a diagnostic probe for these flavonols. Viceversa, flavonol fluorescence provides a very sensitive signal for the presence of metal ions. It also explains the light-fastness of the colorant on textiles dyed using a mordant, since the absorbed light is given up as emission, thus reducing possible photochemical degradation processes.

In conclusion, an alkaline environment, and much more the presence of chelating agents, transform molecules which are not (or poorly) fluorescent and weakly yellow colored into efficient fluorophores and intensely yellow colored materials.

The results here reported can be generalized to the whole wide class of naturally occurring yellow flavonols.

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