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Hydroxyapatite and Alizarin sulfonate ARS modeling interactions for textile dyes removal from wastewaters

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Abstract

Huge amounts of dyes-containing wastewaters are discharged into the environment sometimes without any remediation or land filled as sludges which are difficult to handle and eliminate whatever the method of treatment used.
Due to the lack of reliable data on the structural diversity of these harmful compounds, further information is needed about the retention mechanisms especially on synthetic or natural mineral adsorbents like hydroxyapatite HA, a friendly ecological compound commonly found in soils as phosphate rock.
We already showed the potential use of hydroxyapatite HA to remove textile dyes from various industrial waste water by coprecipitation with HA which could be thereafter regenerated and reused following repeated dye removal by thermal treatment.
As the dihydroxyanthraquinone Alirarin or its salt (ARS) is regarded as a model compound for more complex dyes, this led us to investigate the way calcium ions interact simultaneously with phosphate and ARS. The interaction of ARS with hydroxyapatite (HA) was shown to proceed by formation of whether catecholate salt formation or akin to chelate formation with a phenolic hydroxyl group and adjacent quinone oxygen as already mentioned in the literature. However important details point to a situation more complex than simple adsorption. To clarify the mode of action of HA on the removal of dyes or organic matter in general, we investigated the interactions of alizarinsulfonate ARS with calcium and phosphate ions in solution as a function of pH and dye/adsorbent ratio.
The possibility of the formation of mixed complexes of the type phosphate-calcium-dye which reveals the competition for calcium ions between phosphate and organic ligands is emphasized and reported herein.

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Keywords: Alizarin Sulfonate – Chelation Hydroxyapatite – Textile dyes – Wastewaters;

1. Introduction

Hydroxyapatite (HA) is more than an adsorbent and is capable of forming strong bones in mammals, and protecting teeth with hard enamel despite its simple composition based on calcium and phosphate ions. Many of the complex biological properties of HA are related to the multiple exchange capacities inside the HA structure, including formation of vacancies to accommodate ions with other valencies, in particular carbonate ions and alkali and other metal ions of biological importance.

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Alizarin has long been used for the biological staining of bone tissue, and the interactions between the dye and the HA mineral has been the subject of much scrutiny. The adsorption of alizarin red has long been used to assess the performance of the apatite before use in a water treatment facility. Today, the production includes a wide assortment of colored dyes resistant. Anthraquinone acids are the most important raw materials for the synthesis of these dyes. Anthraquinone dyes are as a business perspective the most important after azo dyes. Their general formula derived from anthracene, shows that the chromophore is a quinone nucleus which can attach hydroxyl or amino groups. These products are used for dyeing polyester fibers, acetate and cellulose triacetate. The structure of alizarin marked the beginning of the anthraquinone chemistry.

Mordant dyes such as alizarin generally contain a functional ligand capable of reacting strongly with aluminum, chromium, cobalt, copper, nickel, or iron salts to give different colored complexes with the textile [1].

Alirarin red sulfonate (ARS) sodium 3-alizarin-sulfonate (also called Alizarine Carmine, Alizarine Red S, Alizarine S) is a typical dihydroxyanthraquinone that has been used as a traditional dye originally derived from the roots of plants of the madder genus. It may be used to identify calcium in tissue sections, as a histochemical stain for calcium in bone tissues. However, it also reacts with magnesium and other alkaline earth elements.

ARS was shown to adsorb on calcite and apatite minerals and modify their flotation properties with oleic acid. [2].

Alizarin Red S (1,2-dihydroxy-9,10-anthraquinone-3-sulfonic acid $ARSH_2$, is considered as a diacid pK (2-OH)= 5.49 and pK(1-OH) = 10.85.

A recent paper reported that electrochemical reduction of the anthraquinone group leads to 1,2,9,10-tetrahydroxy-anthracene-3-sulfonate. According to these authors, there are many species depending upon solution pH and redox potential: three species of the oxidised form of Alizarin Red S are present ($ARSH_2$, $ARSH^-$ and ARS^{2-}), the reduced forms being the five species ARH_4, $ARSH_3^-$, $ARSH_2^{2-}$, $ARSH^{3-}$ and ARS^{4-} (Turcanu and Bechtold, 2011) [3].

Several structures have been proposed for the binding of alizarin red sulfonate (ARS), implying deprotonating of phenolic hydroxyl groups and formation of calcium chelates. As mentioned above, the interaction of ARS with hydroxyapatite (HA) was previously recognized to proceed by formation of a 1 to 1 calcium salt of formula $Ca(ARS).2H_2O$ and release of phosphate ions (D.N.Misra, 1992) [4].

Actually, the doubly deprotonated ARS forms a 1 to 1 calcium complex Ca(ARS) while the monodeprotonated $ARSH^-$ forms a 1 to 2 complex $Ca(ARSH)_2$, as shown by the Figure 1.

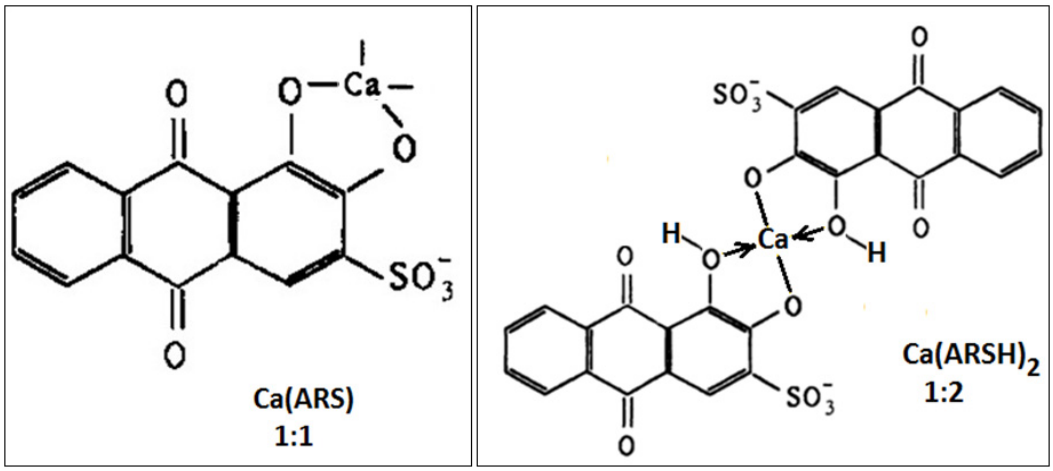

Fig.1: Possible structures of (1 to 1 and 1 to 2) calcium-ARS complexes.

The monodeprotonated ARS forms a 1 to 2 complex $[Ca(HARS)_2]$ with calcium with a log K formation constant of 8.04 in 0.1 M NaCl medium. The doubly deprotonated ARS forms a 1 to 1 calcium complex [CaARS].

On the other hand, Moriguchi claimed two types of bonding of ARS could be observed on HA, one involving diphenolate or catecholate salt formation with 2 phenolic hydroxyl groups, the other akin to ketophenolate akin to chelate formation with a phenolic hydroxyl group and adjacent quinone oxygen (Moriguchi 2003) [5] as shown by the Figure 2.

ARS was found to adsorb on fluoroapatite (Forsling 1993) [6]. The formation constants of ARS with calcium were determined (Wu, 1992) [7].

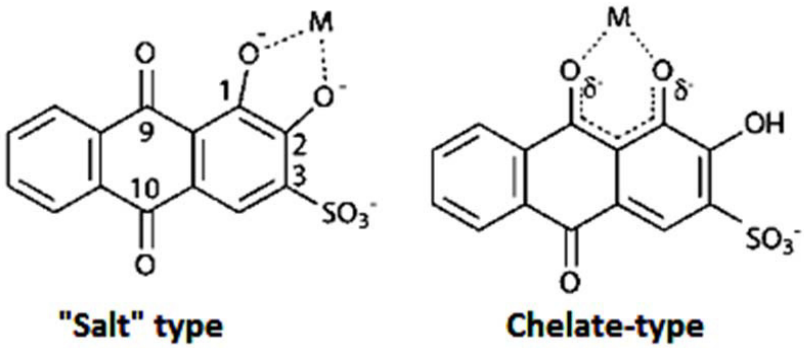

Fig.2: Binding schemes according to Moriguchi et al., also reported by Ibsen and Birkedal [8].

The monodeprotonated ARS forms a 1 to 2 complex with calcium with a log K formation constant of 8.04 in 0.1 M NaCl medium. The doubly deprotonated ARS forms a 1 to 1 calcium complex. The complexation mechanisms reported in the literature never involve participation of the sulfonate group ($-SO_3^-$) of the alizarin-sulfonate ARS.

Ibsen and Birkedal have already reported the effect of the increasing concentration of alizarin red S on the biomineralization of bone-like carbonated apatite nanocrystal formation, leading to a strong stabilization of the amorphous precursor phase [8]; they also support the schemes given by Moriguchi et al. [5] for the two possible complexes formed with apatite as salt or chelate form given above, even though we think that this differentiation could be contestable since the salt form is also a complex and the pentacycles are the most stable chelates.

Because we also previously found that formation of calcium phosphate precipitates in the presence of textile dyes could conveniently eliminate the dye from industrial waste waters, we were interested in the reaction of ARS with calcium in the presence of phosphate. HA was found to be an effective adsorbent that could be regenerated and reused following dye removal by thermal treatment.

We have recently illustrated the possibilities of using HA to remove various textile dyes from industrial waste waters by co-precipitation with HA. Most dyes can be treated efficiently and the HA adsorbent can be regenerated for reuse following thermal treatment in air to burn of the organic materials adsorbed. However two facts point to a situation more complex than simple adsorption: When the HA precipitate is regenerated, a loss of material is observed, small but consistently of the order of 10 to 12%, indicating that part of the HA remains in solution and is not recovered in the precipitates. This loss is higher than that expected by the low solubility product of HA at neutral pH values.

Furthermore, thermogravimetric analysis of the solids revealed organic matter contents reaching over 50% by weight, indicating that the precipitating solids could be formed by some kind of insoluble calcium salt of the dyes with a stoichiometry compatible with the presence of less than 50% minerals.

In the case of ARS, the formation of a $Ca(ARS)_2$ complex was established by potentiometric titrations. We also observed that the presence of several dyes in solution prevented or retarded the precipitation of HA from aqueous solutions even near neutral pH values.

To elucidate the mode of action of HA on the removal of dyes or organic matter in general, we investigated the interactions of ARS with calcium and phosphate ions in solution as a function of pH and dye/mineral fraction.

We report here the observation of the formation of mixed complexes of the type phosphate-Ca-dye which demonstrate the competition for calcium ions between phosphate and organic ligands.

The alizarin dye is therefore a good representative model of industrial organic pollutants as it is an anionic dye which is part of widely used in natural fiber fabrics, wool and cotton textiles. Alizarin is a model compound for more complex dyes, which led us to investigate the way calcium ions interact simultaneously with phosphate and ARS.

Phosphates interfere with alizarin since their presence prevents the dye from attaching to the surface of apatite.

Alizarin was indeed a good affinity for calcium but not enough to dissolve as a soluble form, so there would be formation of a chelate complex by reaction of calcium on the surface of apatite with adjacent OH groups of alizarin. But we also know that alizarin is adsorbed on hydroxyapatite as it is used in histochemistry for staining bone tissues.

This "apparent" competition between the two adsorption schemes is actually an advantage since it allows a synergistic retention of alizarin, alone or within its complexed forms by the sorbent hydroxyapatite HA. As expected from the structure formulae of alizarin red, the pH of is one of the most important factor controlling the adsorption of dye on to the adsorbent. HA was also found to be an effective adsorbent that could be regenerated and reused following dye removal by thermal treatment.

2. Materials and methods

Titrations were performed with a Metrohm titrator equipped with Tiamo software, using a combined glass pH electrode, in a thermostated 20 mL flask protected from atmospheric CO_2 and using purified distilled water (MilliQ quality).

Calcium chloride and phosphoric acid were of analytical grade (VWR) and alizarin sulfonate sodium salt was from Merck.

Ca and PO_4 concentrations were kept in the 1.5 ratio corresponding to tricalcium phosphate.

ARS was titrated alone or in the presence of Ca or (1.5 Ca + 1.0 PO_4), starting at acid pH values. Only the results starting above pH = 7 are illustrated here for better clarity.

The titrations were carried out at a constant rate of sodium hydroxide addition of 1mL/5mn, and under permanent magnetic stirring of the solutions.

3. Results and discussion

Assuming pK values (pK (2-OH) = 5.49 and pK(1-OH) = 10.85) of the diacid alizarin sulfonate given by Wu and Forsling [6, 7], we have drawn the theoretical distribution diagram of alizarin sulfonate (ARS) in the Figure 3 together with that of phosphate system.

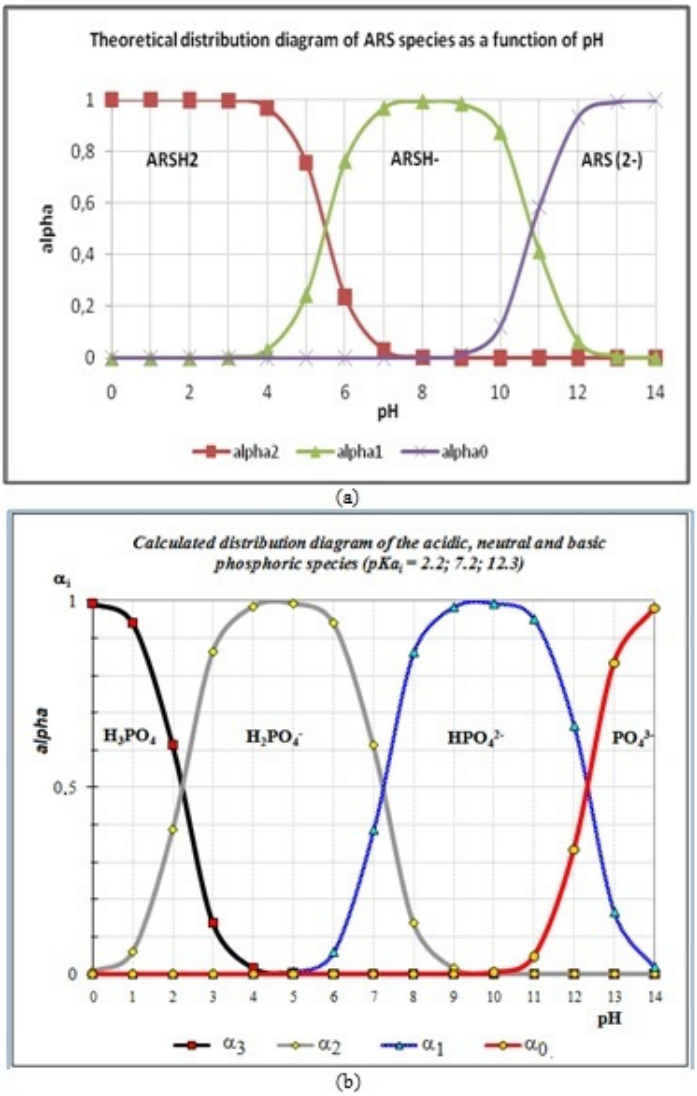

Fig.3: Calculated distribution diagrams versus pH of (a) alizarin sulfonate (ARS) and (b) phosphate species.

Moreover, the ARS dye changes its color with the variation of the pH. We evidenced that by the UV spectrum given for different pH ranges (see Figure 4) and the maximum absorption wavelengths obtained were as follows:

- Yellow color at pH 1.53-3.5 for λ = 420 nm
- Orange color at pH = 4.26 for λ = 423 nm
- Brown red color at pH = 5.43-5.8 for λ = 514-517 nm
- Pink color at pH = 7-8 for λ = 520 -535 nm
- Violet color at pH = 9-11 for λ =543-595 nm

Since the dye alizarin red (ARS) changes its color by increasing the pH, the dye solutions should be analyzed by a UV-VIS in a strongly acidic pH (pH = 2: stable yellow coloration).

Mixing dissolved HA into the alizarin solution and starting at acidic pH values, it was found that most of the pigment is adsorbed when the HA forms a gel as the pH rises to pH 7, reaching 99 % for 1:1 alizarin-HA concentration ratio when the pH rises to pH 10.

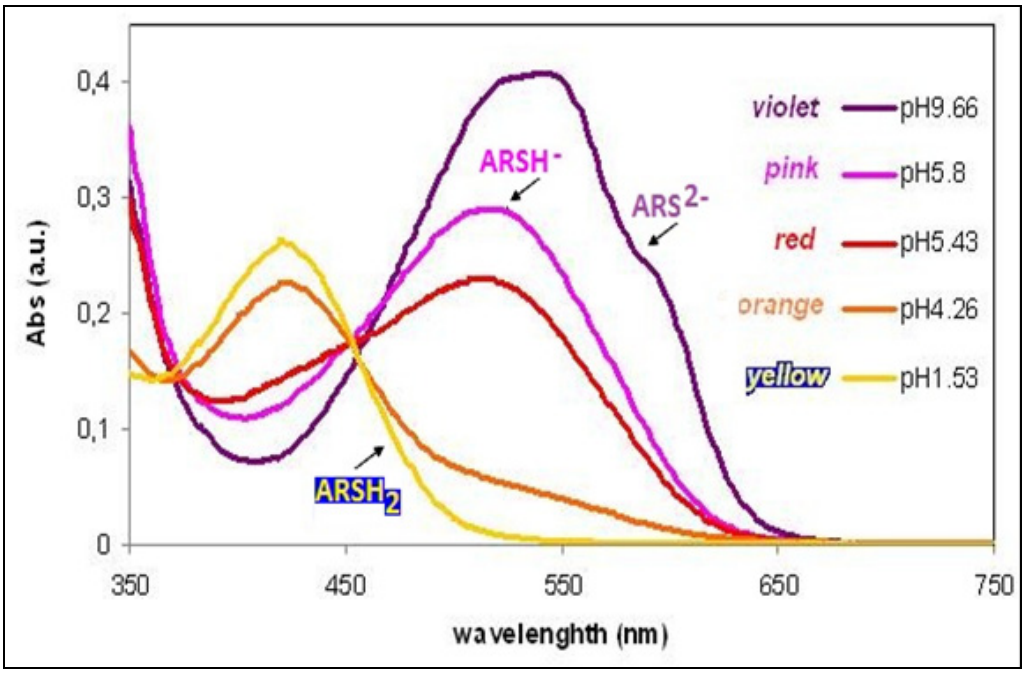

Fig. 4: ARS UV experimental spectrum for different pH values after addition of NaOH to 0.0001M ARS solutions.

[Experimental curves depicted as: Yellow at pH1.53; Orange at pH4.26; Red at pH5.43; Pink at pH5.80; Violet at pH9.66]

A very similar theoretical spectrum has been given by Turcanu and Bechtold [9] for numerous pH values.

As expected from the structure formula, the pH was evidenced as one of the most important factors controlling the adsorption of dye on to the adsorbent, as the alizarine and/or the ARS appear to be a weak acid compound.

Our results using a pHmetric titration study of the systems within variation of parameters like concentration ratios showed a typical behavior of acidity exaltation of weak acids within a formation of complex forms which enhance the acidity strength.

Indeed, the figure 5 and 6 showing the synergetic titration of the weak acids (ammonium, boric acid, …) using complexation with a polyol (glycerol, mannitol, …) could explain the variation exhibited in the figure 7 giving the titration of alizarine-calcium system as well that of the alizarine-calcium-phosphate system when the concentration of alizarin is enhanced, while maintaining constant that of calcium and phosphate.

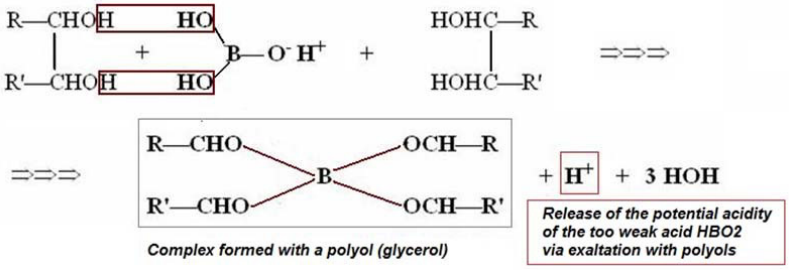

Fig. 5: Release of the potential acidity of (weak) boric acid via exaltation with polyols.

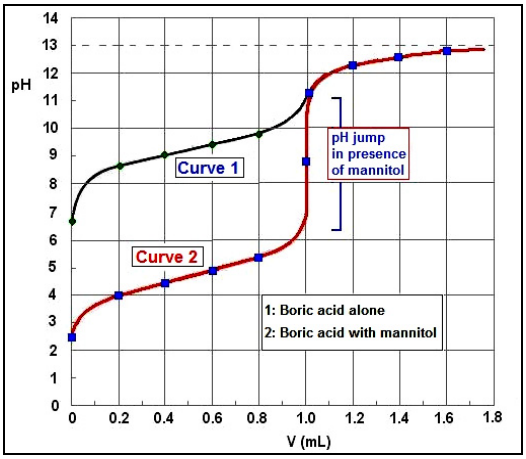

Fig. 6. Synergetic titration of boric acid H_3BO_3 0.1 M by NaOH 1M in presence of mannitol by the Sorensen method.

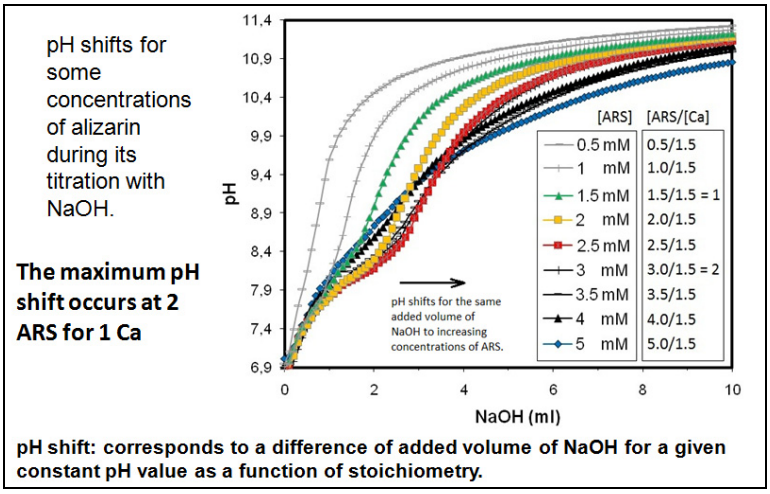

Fig. 7. pH shifts for some concentrations of alizarin during its titration with NaOH

This synergistic effect of the acidity of exaltation is similar to the pH jump shown in the titration curves of boric acid, very weak acid, within complexation by a polyol. For some concentrations of alizarin (for 0.5 mM to 2.5 mM) (figure 7), the pH shift

appears to be significant. The pH shift: corresponds to a difference of added volume of NaOH for a given constant pH value as a function of stoichiometry. It can be seen that the saturation is attained when ARS concentration is 2.5 mM and that there is no more complexation for higher concentrations.

The mixture of alizarin with calcium-phosphate system exhibits a noteworthy behavior when the concentration of alizarin changes from 0.5 to 4 mM, (for constant calcium concentration: 1.5 mM and for constant phosphate concentration: 1.0 mM, therefore for Ca/P = 1.5) (figure 7). One can conclude that the ARS maximal concentration while ARS-calcium-phosphate forms is 2.5 mM at pH =9 and is equal to 2 mM for pH 8 (results not shown).

The maximum $(OH)^-$ shift between the individual curves and the metal-ligand curve occurs at the one to one stoichiometric ratio at pH = 9 with one mole of protons released per mole of ligand. This confirms the formation of [CaARS] complex at this pH value. The pH titrations were performed on Ca/P solutions of TCP stoichiometry (for simplicity, Ca/P =1.5) in the presence of increasing amounts of ARS.

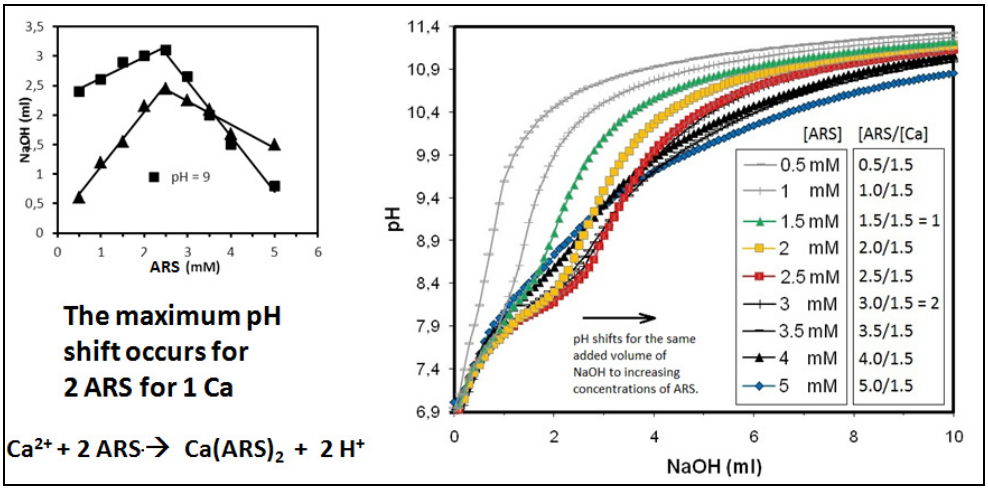

Fig.8: pH shift (or jump) for concentration of alizarin fixed at 1,5 mM during its titration with NaOH.

The mixture of alizarin with calcium-phosphate system exhibits a noteworthy behavior when the concentration of alizarin was equal to 1.5 mM and 3 mM, while maintaining calcium and phosphate concentrations constant and fixed to 1.5 mM and 1 mM, respectively. An illustrative result of titration of 1.25 mm calcium ions in the presence of increasing ARS concentrations is given by the Figure 8.

Significant pH shifts are observed for 1.5 mM ARS concentration and dye excess does not enhance the formation of ARS-calcium-phosphate complex. It obviously appears that the addition of phosphate leads to the apparition of a pH shift due to the formation of complexes enhancing the acidity of both alizarin and phosphate.

This synergetic effect could be exploited to a better retention of wastewaters containing dyes whose structure is similar to alizarine red sulfonate, as it is the case of some textile dyes.

We have therefore focused this aim since our measurements were completed with a series of textile dyes (the HA mass being generally four times the mass of dye) in order to generalize the method using the optimal conditions found with the dye model ARS [10, 11].

5. Conclusion

More than an adsorbent, apatite HA is a reagent whose calcium, hydroxyl and phosphate ions can react with other organic or inorganic species in solution. As alizarin or its salt ARS is regarded as a model compound for more complex dyes, it is interesting to study the way calcium ions interact simultaneously with phosphate and ARS.

Our previous works proved the potential ability of hydroxyapatite to remove many textile dyes from various industrial wastewaters by coprecipitation with this available biosorbent which can be regenerated for reuse after heat treatment in air to burn organic material adsorbed. The strong adsorption of some dyes on the HA precipitates can be explained by strong interaction between phenolic groups in the organic molecules and the calcium ions as this is the case with alizarin. The

interaction HA-ARS was previously recognized to proceed by formation of a 1 to 1 calcium-ARS salt and release of phosphate ions.

The interactions of ARS investigated with calcium and phosphate ions in solution as a function of pH and dye/mineral fraction let us to make clearer the mode of action of HA on the removal of dyes or organic matter in general.

The occurrence of several dyes in solution thus could prevent or retard the precipitation of HA from aqueous solutions even near neutral pH values. The observation of the formation of mixed complexes of the type phosphate-Ca-dye which is reported here could be argued as a demonstration of the competition between phosphate and organic ligands for calcium ions and for some Ca-P-ARS ratios as a synergetic effect for the retention/removal from industrial wastewaters containing those harmful textile dyes.

References

[1] Bauer C., Jacques P., Kalt A., J. Photochem.Photobiol.A: chem. 140 (2001) 87-92.

[2] Fu E. and Somasundaran P., Alizarin S as a flotation modifying agent in calcite-apatite systems, International journal or mineral processing, 18 (1986) 287-296.

[3] Turcanu A., Bechtold T., pH Dependent redox behaviour of Alizarin Red S (1,2-dihydroxy-9,10-anthraquinone-3-sulfonate) - Cyclic voltammetry in presence of dispersed vat dye, Dyes and Pigments 91 (2011)324-331.

[4] Misra D.N., Reaction of Alizarin Red S with hydroxyapatite: Stoichiometry and surface effect, Colloids and Surfaces 66,(3), (1992),181-187.

[5] Moriguchi T., Yano K., Nakagawa S., Kaji F., Elucidation of adsorption mechanism of bone-staining agent alizarin red S on hydroxyapatite by FT-IR microspectroscopy, Journal of Colloid and Interface Science Volume 260, (1),(2003), 19-25.

[6] Wu L. and Forsling W., potentiometric and spectrophotometric study of calcium and alizarin S complexation, Acta Chemica Scandinavica, 46 (1992) 418-422.

[7] Forsling W. and Wu L., Surface complexation at hydrous fluoroapatite, Aquatic sciences,55(4) (1993) 336-346.

[8] Ibsen C. J. S. and Birkedal H., Modification of bone-like apatite nanoparticle size and growth kinetics by alizarin red S, Nanoscale, 2010, 2, 2478-2486, The Royal Society of Chemistry 2010, http://pubs.rsc.org | doi: 10.1039/CONR00488J, downloaded on 07 October 2011

[9] Turcanu A., Bechtold T., pH Dependent redox behaviour of Alizarin Red S (1,2-dihydroxy-9,10-anthraquinone-3-sulfonate) - Cyclic voltammetry in presence of dispersed vat dye, Dyes and Pigments 91 (2011)324-331.

[10] Lemlikchi W., Sharrock P., Mecherri M. O., Fiallo M., Nzihou A., Treatment of Textile Waste Waters by Hydroxyapatite 3 Co-Precipitation with Adsorbent Regeneration and Reuse, Waste and Biomass Valorization, 2011, DOI 10.1007/s12649-011-9096-0.

[11] Sharrock P, Nzihou A, Lemlikchi W, Mecherri M.O., Fiallo M, Recycling CA-HA adsorbent, 4th International Conference on Engineering for Waste and Biomass Valorisatio, september 10-13, 2012, Porto, Potugal.