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# Response surface methodology for the elimination of humic substances from water by coagulation using powdered *Saddled sea bream* scale as coagulant-aid

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Removal of organic substances from water by coagulation with alum and ferric salts were studied by means of conventional jar-test procedures.

The novelty of this work is the use of powdered *Saddled sea bream* scale as coagulant-aid for enhancing the coagulation process with a low concentration of alum ($Al_2(SO_4)_3{\cdot}18H_2O$).

Performance of usual coagulation process depends on the chemical structure of organic components as phenol (PHL), salicylic acid (SA), phthalic acid (PHA) and humic substances (HS), their initial concentrations, coagulant dose, pH medium, and other operational conditions.

The response surface methodology (RSM) was applied to optimize the coagulation process for the elimination of humic substances from water. Initial HS concentration, alum dose, rapid and slow mixing speed, powdered fish scales (PFS) mass and pH were the factors considered in the design.

A quadratic model was developed to express the removal efficiency of HS (response Y) as function of the six parameters. The high values of $R^2$ and $R^2$ adjusted coefficients verify a good correlation between the observed and the predicted response values.


## 1. Introduction

The presence of natural organic matter (NOM) in drinking water can cause significant problems and degrade the quality of water (Bolto and Gregory, 2007). The humic substances (HS) which are the main constituents of NOM become a focus of attention apart from the esthetic problems of color, taste and odor, its presence causes a health hazard because of the formation of potentially carcinogenic chlorinated during water chlorination the well known problem of disinfection by products (DBPs) (Duan and Gregory, 2003; Gregor et al., 1997; Liu et al., 2009). Although enhanced coagulation is considered to be among the best available techniques for the removal of DBPs precursors (Matilainen et al., 2010). Three mechanisms i.e. charge neutralization, entrapment, and adsorption have been demonstrated to exist during coagulation (Duan and Gregory, 2003; Gregor et al., 1997; Li et al., 2006). The most widely used coagulants in water treatment are aluminum and iron salts owing to their high efficiency while synthetic and natural organic polymers, find application too (Simate et al., 2012; Yin, 2010). However, most of the synthetic coagulants are hazardous and can cause environmental and health problems. For example, high concentration of alum may lead to Alzheimer's disease (WHO, 2006; Wu et al., 2012). Fe-salts

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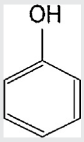
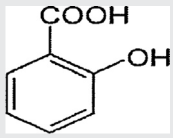
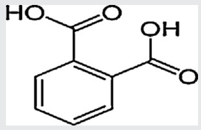
**Table 1 – Chemical and physical properties of organic compounds.**

| Organic compounds | Phenol (PHL) | Salicylic acid (SA) | Phthalic acid (PHA) |
|---|---|---|---|
| Formula | $C_6H_6O$ | $C_7H_6O_3$ | $C_8H_6O_4$ |
| IUPAC name | Phenol | 2-Hydroxybenzoic acid | Benzene-1,2-dicarboxylic acid |
| Molar mass (g/mol) | 94.11 | 138.13 | 166.13 |
| Density (g/cm$^3$, 20 °C) | 1.06 | 1.443 | 1.593 |
| Hydro-solubility (g/L, 20 °C) | 90 | 2.0 | 5.74 |
| Characteristic wavelength (nm) | 270 (Fan et al., 2008; Gonzalez et al., 2007) | 297 (Cathalifaud et al., 1997; Gonzalez et al., 2007) | 235 (Cathalifaud et al., 1997) |
| Chemical structure |   |   |   |
| PKa | 9.89 (20 °C) | 2.97 and 13.6 (20 °C) | 2.89 and 5.41 (25 °C) |

can be costly and the resultant excessive iron may cause unpleasant metallic taste, odor and color, corrosion, foaming or staining (Matilainen et al., 2010; Wu et al., 2012).

Thus, in recent years, there has been considerable interest in the development of biomaterial to become an alternative for conventional coagulants. Several studies referred to the use of alternative coagulants from recyclable materials, due to their cost effectiveness and good removal performance (Poumaye et al., 2012; Ravi Kumar, 2000). Fish scales can be an alternative adsorbent used as coagulant-aid, because of the presence of specific chemical groups of hydroxyapatite (HAp), such as hydroxyl, phosphate and carbonate. Recently, the HAp ($Ca_{10}(PO_4)_6(OH)_2$) is considered to be an interesting sorbent in the purification of waste water (Gómez-Morales et al., 2013) and removal of a variety of heavy metals from aqueous solution (Corami et al., 2008a; Rey et al., 2007). These valuable properties of HAp which include high removal capacity, low water solubility, availability, low cost (Rey et al., 2007), ion exchange property and adsorption affinity bring about the possession of high stability and affinity ions exchange media (Kongsri et al., 2013). Further, few reports described the adsorption of organic molecules on powdered fish scales (Gómez-Morales et al., 2013; Rey et al., 2007). In this work powdered fish scale was used as a new potential coagulant-aid for the elimination of HS from water with coagulation process and there are no other relevant studies with which to compare the present study.

In general, the lower the mineral concentration, the softer the water is. In this research, the powdered fish was used to prevent the high doses of alum during the coagulation process.

This biomaterial was used at a very low quantities and it can be considered as a safe natural product for water treatment

The performance of the coagulation process depends on many factors such as the characteristics of raw water, type of coagulant, pH, and coagulant dose (Duan and Gregory, 2003; Franceschi et al., 2002; Poumaye et al., 2012). The experimental design methodology (RSM) was used to identify the effective parameters and optimize the response with a minimum number of experiments (Goupy and Creighton, 2006; Zularisam et al., 2009). Analysis of variance (ANOVA) provides the statistical results and diagnostic checking tests which enables researchers to evaluate adequacy of the model (Goupy, 2005; Trinh and Kang, 2011).

The main objectives of this study are: (i) the evaluation of the coagulation process performance using two usual coagulants ($Al_2(SO_4)_3{\cdot}H_2O$ and $FeCl_3{\cdot}6H_2O$) for organic compounds: phenol (PHL), salicylic acid (SA), phthalic acid (PHA) and more complex compounds: the humic substances (HS); (ii) the exploration of using powdered fish scales (PFS) as an adsorbent for the elimination of HS from water in batch system and; (iii) the performance of Central composite design for the determination of the effects of six factors (initial HS concentration, alum dose, rapid and slow mixing speed, PFS mass and pH) on the removal efficiency of HS in water and searching optimum conditions.

## 2. Materials and methods

### 2.1. *Organic matter*

Four organic molecules were selected for the coagulation study. Humic Substance was purchased from Humat Star80-Almedsa Agrochimic-Algeria, PHL from Biochem the Chemopharma-USA, SA from BDH, and PHA from Riedel-of HAEN AG Seelze-hannover-Germany. Some chemical and physical properties of PHL, SA, PHA and HS are reported in Tables 1 and 2 respectively and a hypothetical structure of HS is shown in Fig. 1.

### 2.2. *Coagulants*

In this study, two usual coagulants were used: Alum ($Al_2(SO_4)_3{\cdot}18H_2O$; analytic reagent) purchased from Sigma–Aldrich, USA and Ferric chloride ($FeCl_3{\cdot}6H_2O$; analytic reagent) purchased from chemopharma, United Kingdom.

Stock solutions of alum and ferric chloride were prepared with a concentration of 10 g/L and stored in 4 °C.

**Table 2 – Composition of humic substances (HS) used in this study.**

| | | | | | |
|---|---|---|---|---|---|
| Total organic matter | 85% | Fulvic acid | 15% | $H_2O$ | 15% max |
| Total humic extract | 80% | Magnesium | 0.29% | pH | 8-10 |
| Humic acid | 65% | Calcium | 1.3% | Iron | 0.3% |
| Solubility in water | 100% | $K_2O$ | 8% | | |