

**STUDY OF ELIMINATION AND INFLUENCE
OF REACTION PARAMETERS ON ALUMINIUM SULFATE STOICHIOMETRY /
PESTICIDE RIDOMIL-GOLD
66WP IN AQUEOUS SOLUTION**

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Abstract

The objective of this study is to establish a stoichiometry between the coagulant and organic matter using reaction parameters that are derived from physicochemical process -flocculation the coagulation. Aluminium sulfate which is a commonly used coagulant in water treatment was tested. Jar-tests were performed on solutions of Ridomil-Gold 66WP pesticide obtained by dissolution. The influence of various parameters were studied, notably the concentration of the solution at different pH media. The results obtained at the end of the treatments performed at pH = 5, 7, 9 are respectively (100; 98.30; 99.55) % removal rate of Ridomil Gold-66WP at variable concentration (20, 50, 100, 200, 250) mg / L.

These concentrations were tested with varying doses of aluminium sulfate (0.25, 0.5, 0.75, 1, 1.25, 1.5 and 1.75)g. The results show that the efficiency of the process and the coagulant assay depend on the pH of the reaction medium and the initial concentration of compound. Stoichiometry reactions laws which gives a relationship between the dose of coagulant to the initial concentration of Ridomil Gold-66WP depend essentially on the pH of the reaction medium.

Keywords: Gold -Ridomil 66WP, Coagulation-Flocculation, Aluminium sulphate, Abatement, Stoichiometry.

1. Introduction

Water pollution in general and that caused by the presence of pesticides in particular is a major challenge for organizations working in this sector. That is why researchers, water treatment companies and organizations fighting for the protection of the environment are joining forces to set up a relatively complete method to fight pollution. Water pollution caused by pesticides is directly related to their application. Unfortunately during the spraying process, about 25 to 75% of these pesticides do not reach their target [1]. An important part of widespread pesticide is dispersed into the atmosphere, either by evaporation on contact with heat or from the plants, and this causes a strong contamination of the air, fog, groundwater, surfaces and rain water. Pesticides can also be found in soil on which they were dispersed. Sometimes they are scattered far from their place of application, and are brought directly to bodies of water and soil by rain. They are then carried away by runoff, infiltration, land leaching or by rainwater leaching into aquatic environments and groundwater. This is why some countries in collaboration with their Ministries of Agriculture, Environment and their Institutes of Agricultural Research have developed a collective scientific expertise taking stock of the available knowledge on the conditions of use of pesticides in agriculture, ways of reducing their applications thus limiting environmental impacts.

This work is a contribution to the elimination of pesticides responsible for the instability of the water quality over time. In conventional water treatment sectors, coagulation-flocculation can significantly reduce these pesticides despite their dissolved state, followed by clarification. It is a process whose efficiency depends on the composition of the aqueous medium, the nature of the coagulant introduced as well as the structure of the compound to eliminate the particular functional groups [2]. This study is to establish the stoichiometric ratio between the optimal doses of coagulant and the initial concentration of a fungicide commercially known as Ridomil Gold 66WP. This compound consists of a mixture of metalaxyl (6%) and copper (I) oxide (60%). Jar-tests trials were focused on solutions of Ridomil-Gold 66WP dissolved in distilled water with variable reaction parameters (initial concentration of the compound, coagulant dose, pH).

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Our study was carried out on several types of pure fungicide solutions, provided a company selling chemicals (Riedel del Haen). It is from Ridomil Gold-66WP (pink powder dissolved in distilled water) that all synthetic solutions of the various desired concentrations were prepared. A stock

solution of 500mg / L was prepared, and then successive dilutions of 20, 50, 100,150, 200 and 250 mg / L were obtained. The choice of coagulant used was according to SANJA PAPIĆ [3] on coagulation of several organic compounds. In this case, aluminium sulfate octadecahydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) of varying doses (0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75) g was used as coagulant. pH adjustments, were made using H_2SO_4 solution (98%) and NaOH (0.1N).

2.2. Analytical Method

The absorbance (A) of Ridomil Gold-66WP solution was measured using a Aqualytic Spectro-Direct Spectrophotometer. The maximum absorption wavelength used was 499 nm, obtained by scanning between 330 and 900nm. Residual concentrations were determined from calibration curves established previously. The removal efficiency was obtained by the following relationship :

$$\text{Abatement (\%)} = \text{R (\%)} = \frac{C_0 - C_f}{C_0} \times 100$$

C_0 and C_f represent respectively the initial and final concentrations of Ridomil Gold-66WP in aqueous solution.

2.3. Jar-test

The coagulation-flocculation tests in this study were conducted following the experimental mode of "Jar test" with 6 magnetic stirrers that allowed simultaneous agitation of solutions containing Ridomil-Gold 66WP and coagulant. The solutions are subjected to vigorous stirring (800tr / min) for 10 minutes, then to a slightly reduced speed (40tr/ min) for 3 min. A pH meter (HANNA brand H19811-5pH/° C/ TDS) was immersed in the solution, then an amount of sulfuric acid or sodium hydroxide is introduced to adjust the pH to the respective values of 5, 7 and 9. After a settling period ($t = 60\text{min}$), the supernatant was collected and analyzed by spectrophotometer [4].

The correlation between the initial content of this pollutant and the coagulant used was established by varying the initial concentrations of Ridomil-Gold 66WP in distilled water solution and then coagulating with increasing doses of aluminium sulfate.

3. RESULTS AND DISCUSSIONS

The following results show the coagulation flocculation on Ridomil Gold-66WP for different concentrations of the solution and coagulant doses at varying pH.

3.1. Direct observation during the elimination in aqueous solution

The evolution of the curves illustrated in Fig. 1 shows the existence of a strong gradient for elimination of coagulant at dose $m = 0.25g$. It should be noted that for $C_1 = 20mg / L$ and whatever the pH, the percentages of abatement give a zig-zag like curve with increasing dose of coagulant. For $m = 1.75g$ dose and $20mg / L$, the reduction rate obtained is 50%, 84.78% and 73.91% respectively for $pH = 5, 7$ and 9 . In addition, at the same pH values for $C_2 = 100mg / L$, we obtain a plateau beyond $0.25g$ ($0.5 - 1.75g$), which corresponds to a pseudo-equilibrium which implies almost total elimination of the pesticide solution (100% reduction). Note also that for the Ridomil Gold-66 WP, the best removal rate in solution by coagulation with aluminium sulfate is obtained at neutral pH ($pH = 7$).

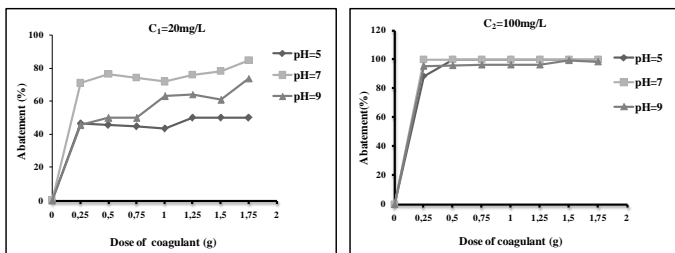


Fig. 1: Evolution of removal efficiency in concentration at varying pHs with different doses of coagulant ($C_1=20mg/L$ and $C_2=100mg/L$)

The presence of a strong gradient of elimination for $m = 0.25g$ is also observed for the concentrations $C_3 = 150mg / L$ and $C_4 =$

$200mg / L$. From Fig. 2, increasing the concentration of pesticide in solution, results to an increase in the removal rate for $0.25g$. For this mass, the change in pH did not influence much the coagulation treatment, because we reached abatement rates quite close to 95%, both for $150mg / L$ and $200mg / L$. Beyond this mass, neutral pH treatment ($pH = 7$) seems to be most appropriate to carry out coagulation of Ridomil-Gold 66WP in aqueous solution.

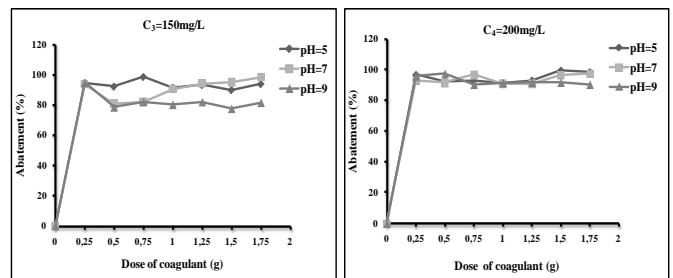


Fig.2: Evolution of removal efficiency in concentration at varying pHs with different doses of coagulant ($C_3=150mg/L$ and $C_4=200mg/L$)

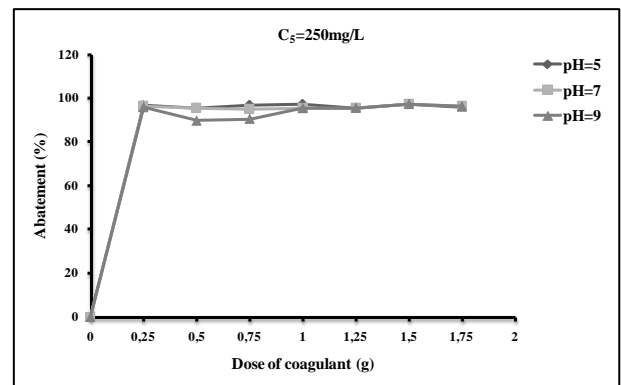


Fig. 3: Evolution of removal efficiency in concentration at varying pHs with different doses of coagulant ($C_5=250mg/L$)

Fig.3, similarly to the others, highlights the effectiveness of treatment by coagulation with aluminium sulfate. The strong growth rate of abatement at 0.25g is also observed. There is a pseudo - equilibrium moved beyond this critical mass ($m = 0.25g$). Between 0.5 and 1.75g a removal rate of about 96% is mostly reached for acidic, neutral and basic pHs.

3.2. Mechanism of coagulation-flocculation of Ridomil-Gold 66WP at different pH

In general, we found that for all the work done at pH values between 5 and 9 and for all concentrations tested (20 to 250mg / L), the Ridomil-Gold 66WP elimination yields were satisfactory according to fig.1. This high removal efficiencies of the compound is due to the size and the high molecular molar mass of the different fractions of the compound [5].

Moreover, it appears from Fig.1 that, Ridomil-Gold 66WP is poorly removed at pH 5 and $Co = 20mg / L$. The yield obtained in this case varies between 49-50%, which seems low compared to other results.

Furthermore, for all other concentrations and pH, the yields vary from 76 to 100%, which is better than those obtained at pH = 5. For the case of pH = 5 and $Co = 20mg / L$ where the removal efficiencies were low, it can be attributed to the fact that the dominant hydrolysed aluminium species are anionic complexes such-soluble $Al(OH)_4^-$ and $Al(OH)_5^{2-}$ difficult to decant with the formation of aluminium hydroxide.

Ridomil Gold-66WP molecules would dissociate providing negatively charged derivatives that produce a repulsion with anionic complexes $Al(OH)_4^-$ and $Al(OH)_5^{2-}$. Also, this can also be explained by a competitive complexation of OH anions present in solution with aluminium. Therefore, it is in favor of the formation of organo-aluminium products rather insoluble by complexation mechanisms of organic compounds with anionic soluble forms [6]. Previous work on the coagulation-flocculation of different simple aromatic compounds lead to results which confirm that, contrary to the hydroxyl groups (-OH), carboxylic groups (-COOH) may play a very important role in the elimination in aqueous solution organic compounds [7]. For pH 7 to 9, and at all concentrations ($Co = 50$ to $250mg / L$) via the pH = 5, we see an increase in removal efficiencies ranging from 76 to 100%. At these pH relatively and at the concentrations tested, hydrolysed

species are aluminium floc comprising a mixture of $\text{Al}(\text{OH})_3$ amorphous and soluble cationic positively charged species such as $\text{Al}(\text{OH})^{2+}$ et $\text{Al}(\text{OH})_2^+$ which could qualify the mechanisms of coagulation-flocculation. Therefore, it favours the predominant formation of organo-aluminium products [8].

Previous work on the coagulation-flocculation of aluminium by similar organic compounds, have shown that the improved results can be attributed to the fact that there is a competition between the surface complexation by organic compounds and polymerization reactions of the aluminium hydroxide.

3.3. The study of stoichiometric laws at different pH

The method of linear least squares allows pairs of adjustment values of the two reaction parameters, namely: the optimum dose of the coagulant ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) and the initial concentration of Ridomil Gold-66WP to achieve linear stoichiometric relationships. The correlation coefficient values were obtained with expressions of Law at different pH of the reaction medium of commercial pesticide.

Fig.4 illustrates the case at $\text{pH} = 5$ and indicates a stoichiometry of 145mg of aluminium sulfate per mg of Ridomil Gold-66WP. This result shows that, at low pH the reaction mechanism between

Ridomil-Gold 66WP and Al^{3+} cations dissolved is well stoichiometric.

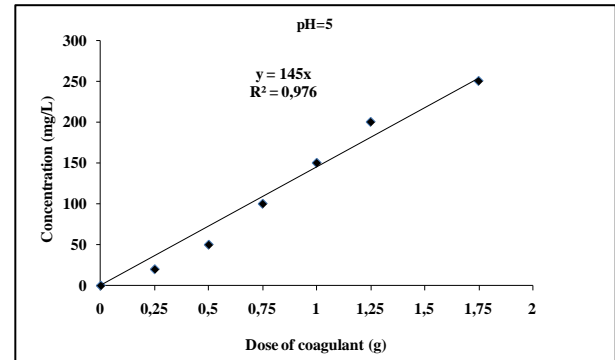


Fig.4 : Relationship between optimal doses of coagulant and the concentration of Ridomil Gold-66WP to $\text{pH} = 5$.

Agreably this result confirms that obtained in the previous study of the stoichiometry between the coagulant dose and the concentration of a carboxylic acid derivative in the pH range between 4 and 6, for the same performance elimination, high doses of aluminium would be required beyond pH 6 [9,10].

Fig. 5 is a representation of the stoichiometric law obtained at $\text{pH} = 7$. It also highlights the linear law in relation to stoichiometry established between the dose of aluminium sulfate / initial concentration of Ridomil-Gold 66WP equal to 154.7 mg of aluminium sulfate per mg Ridomil-Gold 66WP. Referring to the previous case, at $\text{pH} = 7$ the application of coagulant is more important.

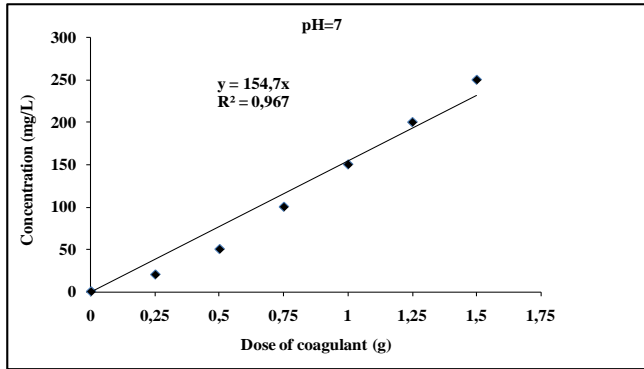


Fig. 5 : Relationship between the coagulant optimum dose and concentration of Ridomil-Gold66WP at pH = 7

Fig.6 represents the stoichiometric law of Ridomil Gold-66WP when its pH is adjusted to 9. The stoichiometry mass ratio is equal to 138mg of aluminium sulfate per mg of Ridomil Gold-66WP.

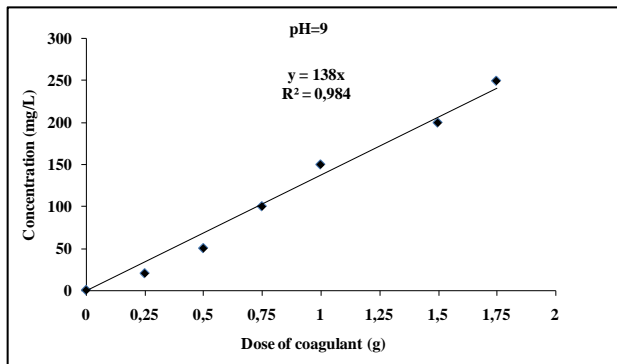


Fig. 6 : Relationship between the coagulant optimum dose and concentration of Ridomil-Gold66WP at pH = 9

The stoichiometric coefficients increases from basic pH to neutral through acidic. This can be explained by the fact that competitive complexation of a significant amount of OH⁻ ion

in combination with the Al³⁺ cations which are in the form Al(OH)²⁺ and Al(OH)₂⁺ become neutral salts of the type Al(OH)R and Al(OH)₂R which are soluble and easily precipitated in the reaction medium.

4. Conclusions

This study is part of the treatment of a fungicide (Ridomil-Gold 66WP) with the aim of establishing the mass ratio of stoichiometry between the initial concentration of Ridomil-Gold 66WP testing the optimal dose of coagulant while following reaction parameters that accompany the amount of aluminium sulfate. We found out during the work that, removal rates improve when the coagulant dose and initial concentration of organic compound increase.

Moreover, the best removal rates are obtained at pH 7 and 9. The reaction mechanisms for different pHs tested appeared to be directly related to the predominant hydrolyzed species of aluminium (BACHA and ACHOUR 2015). Different removal rates obtained, demonstrate the influence of reaction parameters (coagulant dosage, initial concentration and pH) on the amount of the coagulant used in the coagulation-flocculation reactions. This reaction is stoichiometric and is mainly linked to the presence in the molecule of Ridomil Gold-66WP the

carboxyl group (-COOH) on the aromatic structure.

References

[1] V. FRANÇOIS, "Pesticides: the trap closes" edition Living Earth, 2013.

[2] R. DESJARDINS, K. LENGU and S. NDIONGO, (1996). "A comparative study of the performance of various prehydrolyzed coagulants on the removal of dissolved organic matter. " Vector Environment, Vol. 29, 1996, pp 37-45.

[3] S.PAPIC, N.KOPRIVANAC, A.L. BOZIC and A.METES, "Removal of some reactive dyes from synthetic wastewater by combined Al(III) coagulation/carbon adsorption process , Dyes and Pigments ,Vol.62, 2004 , pp 291–298.

[4] H. KHELILI, S. ACHOUR and A. REZEG, "Efficacy of aluminium sulfate and activated carbon in the destruction of aromatic organic pollutants ", Larhyss Journal, Vol.4, 2010, pp.153-168.

[5] N. BACHA, and S. ACHOUR, "Influence of reaction parameters on the stoichiometry Aluminium sulphate / pyromellitic acid in distilled water", Larhyss Journal, Vol.13, 2013, pp.109-123.

[6] N. BACHA, and S. ACHOUR, "Influence of reaction parameters on the stoichiometry Aluminium sulphate / Natural organic matter in distilled water ", Larhyss Journal, Vol.21, 2015, pp.151-158.

[7] S. ACHOUR. and N. GUESBAYA, "Coagulation-flocculation with aluminium sulphate of phenolic organic compounds and humic substances " , Larhyss Journal, Vol. 9, 2005, pp. 99-110.

[8] A. REZEG, "Elimination of hydrolyzed organic acid and carbonyl by coagulation-flocculation with aluminium sulfate ", Ph.D Thesis, Water Science, University of Biskra, Algeria, 2014.

[9] J.K. EDZWALD, J.D. HAFT and J.W. BOAK, Polymer coagulation of humic acids, Water, J. Environ.Eng.Div, ASCE, Vol.103, 1977, pp 989-1000.

[10] J.K. EDZWALD, Coagulation of humic substances, AICHE Sym. series 190, Water, Vol. 75, 1979, pp 54-62.

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1-Estella T. Njoyim, Yves T. Djoko, Julius Ghogomu, **Serge A. Djepang**, Samuel Laminsi . Plasma Chemical Treatment of Industrial wastewater for brewery " Brasseries du Cameroun", Bafoussam Factory. *International Journal of Environmental Research and Applications*. Vol 6, Issue 1, (Part- 4). January 2016, pp. 60-71.

2-Daouda Abia, Gaël Claude Mbafo Fondjo, Elie Acayanka, **Serge Alain Djepang**, Abba Paltahe, Samuel Laminsi & Paul Mingo Ghogomu (2015): Degradation of wastewater from cotton oil refinery by gliding arc plasma at atmospheric pressure, *International Journal of Environmental Studies*, DOI:10.1080/00207233.2015.1108599.

3-P. Abba, **S. Djepang**, S. Laminsi, Jean-Louis Brisset, Eugen Hnatiuc, Bogdan Hnatiuc. Pollution Abatement of Tannery Workshop Effluents. *IEEE TRANSACTIONS ON INDUSTRY APPLICATIONS*, Vol. 51, No. 1, January/February 2015. pp.1066-1069.

4-Serge Alain Djepang, Samuel Laminsi, Estella Njoyim-Tamungang, Cedrik Ngnintedem and Jean-Louis Brisset. Plasma-Chemical and Photo-Catalytic Degradation of Bromophenol Blue. *Chemical and Materials Engineering*. (2014). 2(1): 14-23.

5-Serge Alain Djepang, Laminsi Samuel, Djakaou Iya-Sou, Koyaouili Thierry. Elimination of Black Eriochrome T by Plasma Glidarc. *Journal Of Water Science*. (2014). 27(1) : 71-78

6-Jourdin Gongwala, **Serge Alain Djepang**, Paltahe Abba, Gaston Payom, Samuel Laminsi, Daniel Njopwouo. Treatment of Wastewater from a Slaughterhouse by Gliding Arc Humid Air Plasma: Chlorophyll Degradation. *International Journal Of Environmental Protection And Policy*. (2014). 2(3): 118-125.

7-Fouodjouo Moïse, Laminsi Samuel, **Djepang Serge Alain**, Tadam Doringar and Brisset Jean-Louis. Non-Thermal Plasma Coupled to TiO₂ Applicable for the Removal of Paraquat from Aqueous Solutions. *International Journal Of Research In Chemistry And Environment*. (2013). 3(1): 316-326.

8-Paltahe Abba, Samuel Laminsi, Jean Tarkwa, **Serge Djepang**, Jean Louis Brisset. Non-Thermal Plasma Decontamination Of Tanning workshop



Effluents. *Environmental Engineering And Management Journal*. (2013). Acceptor in October 2013.

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