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Comparison of activated carbon and new granules based on gluten extracted binder: adsorption application and Statistical analysis

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Abstract. Statistical analysis is considered today as a method that is an integral part of each experiment and allows researchers to exploit their results and draw conclusions. Based on statistical analysis, this study focused on analyzing by the PCA method of the effect of some physicochemical properties of a new generation of granules with gluten and of a commercial activated carbon for the adsorption of a green malachite MG, and relationships between them were presented by regression analysis, also concerned the examination of the different relationships that may exist between these different properties. The achieved results indicated that the influence of granule size, porosity, pHzpc, cation exchange capacity CEC, and specific surface area SSA on the adsorption capacity of MG is better; the best removal efficiency was established at small size granules.

Key words: Adsorption, Binder, Dyes, Granules, Statistical analysis.

1 Introduction

In recent years, the production of waste materials has increased due to the growth of industrial activities and demography around the world. Therefore, recycling and reusing these waste materials for different applications would make a tremendous contribution to waste elimination.

Contamination of water and soil resources with leachate from this waste as well as organic and mineral pollutants from agricultural, urban and industrial sources pose a major risk to human health and the environment [1].

Malachite green (MG) as a model pollutant in the textile industry belongs to the class of industrial dyes. It is considered today as a toxic pollutant and dangerous for humans and the environment. The effluents discharged by the textile industries, laden with dyes, in rivers, can significantly affect animal and plant species as well as various microorganisms living in these waters. This toxicity could therefore be linked to the decrease in dissolved oxygen in these media. In addition, their very low biodegradability, due to their high molecular weight and their complex structures, gives these compounds a toxic character which can be high or low. As a

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result, they can persist for a long time in this environment, generating significant disturbances in the various natural mechanisms of flora and fauna [2].

In order to preserve and improve the quality of these resources, traditional treatment techniques have already been implemented in the past.

Over the past two decades, several new methods of destroying pollutants have been developed [3]. In this context, the adsorption seems to be the simple and effective technique for eliminating and / or reducing a wide range of mineral and organic pollutants. Activated charcoal as an absorbent and effective has been used for a very long time because of its large specific surface and its developed porosity. Nevertheless, there are still certain drawbacks linked to losses due to oxidation during the regeneration processes and to the cost [1].

In this field, many researchers have turned rather to the use of natural materials such as natural and / or modified clays [4]. Over the past 20 years, much research has shown that hydrophobic and organophilic modified clays are more effective in sorption of several water-soluble contaminants [4].

Thus, three main families of modified clays have been implemented: Organo-clay complexes (clays pillared by organic molecules), inorganic-clay complexes (clays pillared with inorganic polycations) and organo-inorgano-clay complexes (clays pillared with inorganic polycations and co_adsorbed by organic molecules).

The structural diversity of organo-inorgano-clay complexes called also surfactant-modified pillared-montmorillonites (SMPM) offers the potential to increase sorption capacities. Many studies have focused on using SMPM to eliminate organic pollutants in a wide variety of environmental aqueous solutions [5].

The granulation is defined as a process to recover solid, liquid and gaseous materials in small granules or beads. This technology has been successfully implemented to immobilize adsorbent powders into spherical beads or granules that are easily separable in aqueous solution. Biopolymers have actually become the preferred granulation material by offering the advantages of non-toxicity, high reactivity and affordability, inexpensiveness, as evidenced by silicone [13-18].

The wheat gluten proteins correspond to the major storage proteins that are deposited in the starchy endosperm cells of the developing grain. These form a continuous protein matrix in the cells of the mature dry grain and are brought together to form a continuous viscoelastic network when flour is mixed with water to form dough. These viscoelastic properties underpin the utilization of wheat to give bread and other processed foods. A novel resistant granular sorbents based on iron granular surfactant modified pillared montmorillonite and gluten as binder noted (Fe-GSMPM) are prepared, characterized and used in single, mixture and dynamic adsorption.

The present study was focused on comparing and evaluating the performance of the new Fe-GSMPM granular in the removal of Malachite Green dye from textile wastewater by using principal component analysis noted PCA (Past software) as a statistical analysis model PCA is a statistical procedure that uses an orthogonal transformation to convert a set of observations of possibly correlated variables (entities each of which takes on various numerical values) into a set of values of linearly uncorrelated variables called principal components. It is mostly used as a tool in exploratory data analysis and for making predictive models. It is often used to visualize genetic distance and relatedness between populations.

In order to better understand and correlate the physique data (granules size, Porosity, pHzpc, cationic exchange capacity CEC and specific surface area SSA) of Fe-GSMPM granules with adsorption capacities of MG alone and in mixture at presence of another dye RB with different ratio 3/1, 1/1, and 1/3, we have used the Principal Component Analysis method.

2 Materials and methods

2.1 Fe-GSMPM granules materials

The iron surfactant-modified pillared montmorillonite powder noted Fe-SMPM (size < 50 µm) was synthesized according to the procedures previously optimized [6-8].
The granules noted (Fe-SMPMG) based on an iron organo-inorgano montmorillonite complex SMPMG and gluten (G), as an inert binding agent, was prepared by dry compaction granulation. The optimal granulation conditions are essentially related to the concentration of gluten (40 %) in the mixture as well as to compression between two identical wheels adjustable at a rotation speed of 2.5 rpm for duration of 24 sec.

2.2 Principal component analysis (PCA) technics

In order to correlate the physical properties in relation to the the used components (Activated carbon, Fe-SMPMG, Mt-Fe-CTAB, Mt-Fe, Mt-Na, Bentonite, Gluten) to the adsorption results of MG on Fe-SMPMG granules, we used the principal component analysis (PCA) method using the Past software and the following variables: (granule size, porosity, pHpzc, CEC, SAA), the adsorption quantities (Q) of MG alone and in the presence of another polluting Rhodamine B (RB) with a different ratio r (r=MG/RB= 3/1, 1/1, 1/3), respectively). Indeed, the PCA method allows not only to analyze and compress the experimental data but also to determine their similarities and differences [6], [9-12].

3 Results and Discussion

3.1 Physico-chemical properties

The physico-chemical properties of granules prepared by compaction granulation noted Fe-SMPMG as well as those of the powders of Mt-Fe-CTAB, Mt-Fe, Mt-Na, Bentonite, Gluten and activated carbon are summarized in Table 1. These results clearly show that the pillaring of the clay transforms and modifies its surface properties which become more negative (negative pHzpc) thereby indicating the possibility of these materials to adsorb positively charged species such as those of the MG dye through electrostatic interactions.

Table 1. Physico-chemical properties of the used adsorbents

	Activated carbon	Fe-SMPMG	Mt-Fe-CTAB	Mt-Fe	Mt-Na	Bentonite	Gluten
pHzpc	5.6	5.5	4.4	4.1	2.6	2.1	6.8
CEC (meq/100g)	200	7	7	12	78	65	20
SSA(m^2/g)	950	14	14	120	91	54	10

A decrease in in the cation exchange capacity and in specific surface pHzpc after pillaring indicates that the surface becomes more negative and this helps to adsorb such as MG [2]. The chemical composition of prepared granules obtained by Fluorescence RX spectrometry type "ZSX Primus II de Rigaku" are shown in Table 2.

Table 2. Chemical composition of the new prepared granules (Fe-SMPMG)

Element	C	N	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Br	Fe
% weight	30.23	5.68	40.05	6.94	0.51	2.41	5.33	0.028	0.16	2.16	0.13	0.07	0.01	0.23	5.94

3.2 Statistical analysis

Significant correlations exist between the different parameters studied in terms of granule size, porosity, CEC SSA and pHzpc of adsorbent Grains.

3.2.1 Statistical characteristics

The removal percentage of MG dye is presented for each adsorbent studied, which is presented in as a histogram. These histograms show that the best result is obtained with activated carbon with a percentage exceeding 90%, followed respectively by prepared grains from smaller to larger sizes of 200, 800 and 1200µm. while gluten, bentonite and Mt-Na have the lowest percentage below 10%.

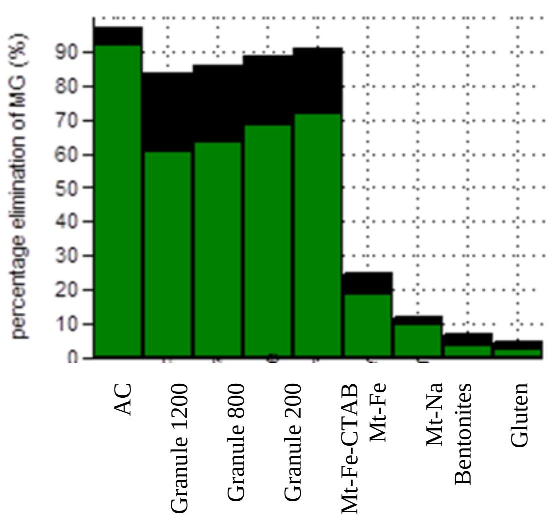

Fig 1. Percentage elimination of MG by adsorbent studies

The histograms in Figure 1 show the percentages of elimination of the MG dye obtained for each studied adsorbent.

These histograms clearly show that the best results are obtained with activated carbon and the smaller Fe-SMPMG grains in the following sequential order.

AC > Fe-SMPMG (200 µm) > Fe-SMPMG (800 µm) > Fe-SMPMG (200 µm) > Fe-SMPM > Mt-Fe. Gluten, crude bentonite and Na-Mt have the percentage the lowest below 10%.

Figure 2 (a), presents the correlations calculated by the PAST software for all the studied parameters of which they are: positive for grain size, SSA, pHzpc, negative for CEC and porosity This is due to the percentage of pollutant removal which is higher for positive correlation. For the (MG / RB) binary mixtures, we found that the best result is obtained for MG alone and begins to decrease as the presence of Rhodamine B increases in the mixture. The adsorption of MG therefore, decreases when the (MG / RB) ratio increases in the range from 3/1, 1/1 and 1/3 respectively. Figure 2, (b) confirms the results calculated in Figure 2 (a), for the quantities of adsorption that which decrease in the MG direction only (Q), (3/1), (1/1) and (1/3).

(a) (b)

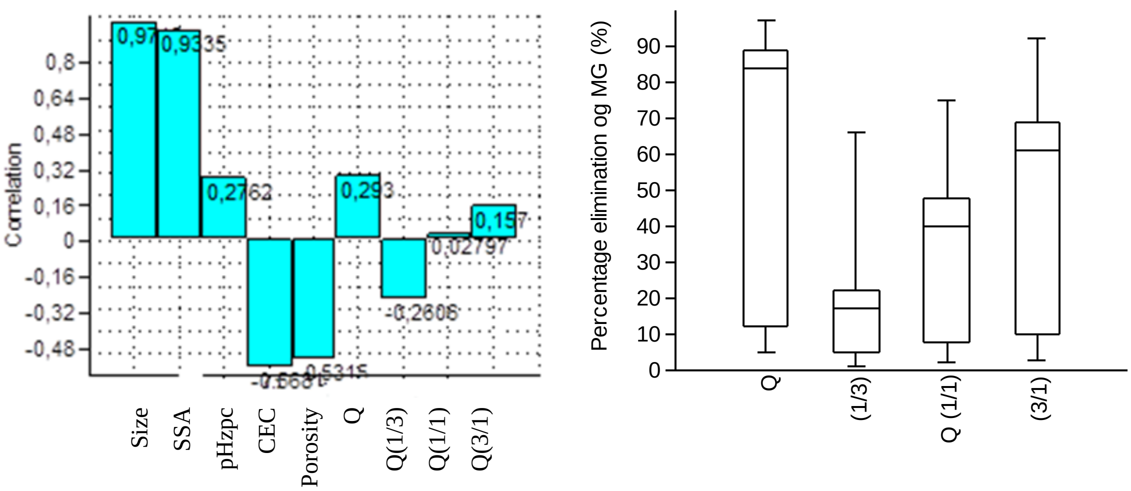

Fig 2. (a) correlation of different parameters; (b) Elimination of MG of different ratios

3.2.2 Principal component analysis

3.2.2.1 Linear correlation

In order to verify the validity of this PCA method, we have used these results with the Past software. This allowed us to perform a linear correlation in order to have a more precise idea of the existing links between the data (variables and responses) taken two by two. The corresponding results are presented in Table 3.

Table 3 Matrix of correlation between the variables and the responses studied.

	Granules size	Porosity	pH_{pzc}	CEC	SSA
Granules size	1				
Porosity	0.935	1			
pH_{pzc}	0.415	0.321	1		
CEC	-0.431	-0.447	-0.788	1	
SSA	0.563	0.690	0.452	-0.711	1

Examination of the correlation matrix reveals the presence of very strong correlations between the pairs: (size of the granules, porosity). This significant correlation between the quantity adsorbed, porosity, and the size of the granules is also supported by a satisfactory correlation coefficient (r = 0.93), also between the adsorbed quantity and porosity, additionally, the size granules, The porosity and the SSA of prepared Fe-GSMPM granules are strongly correlated with the adsorption quantity Q, such as the other data are well correlated with each other: porosity and pHzpc (r = 0.32). The degree of correlation between the CEC and parameters such as size and Q is low (r = -0.43 and r = -0.71, respectively), suggesting that the CEC of Fe-GSMPM is not dependent on these parameters.

3.2.2.2 Variables studies

The contribution of each variable in the formation of the principal component is given here by the correlation coefficient between the variable and the axis considered. As indicated in Table 4, this coefficient is all the more important since the variable contributing to the formation of the axis is important.

Table 4. Coefficients of correlations of data related to the main axes.

	Axis 1	Axis 2	Axis 3	Axis 4	Axis 5
Fe-GSMPM (1200 µm)	-2.694	1.212	-0.535	0.116	-0.006
Fe-GSMPM (800 µm)	-1.861	0.314	-0.048	-0.072	-0.163
Fe-GSMPM powder	-1.073	-0.503	0.570	-0.241	0.385
Mt-Fe-CTAB	-0.239	-0.757	1.201	-0.057	-0.239
Mt-Fe	0.784	-0.574	-0.104	0.762	0.099
Mt-Na	2.263	1.049	-0.121	-0.360	0.056
Raw Bentonite	2.289	0.909	0.133	0.114	-0.057
Gluten	0.531	-1.649	-1.096	-0.260	-0.074

Table 4, which deals with the correlation between the data and the main axes, clearly shows that the variables are rather better represented with the axis 1. In particular, the parameters related to the Fe- GSMPM granules, Mt-Na and Gluten are characterized by a good correlation on the axis 1.

3.2.2.3 PCA graphic representation

As shown in Fig. 4, the PCA method performed on the data set produced two significant principal components PC1 and PC2 which contributes to around 21% and 66% of the total variance in the data set, respectively. The biplot results reveal three distinct groups of granules: The first one (Raw Bentonite and Mt-Na) shows the less good mechanical properties except CEC with the very low adsorption capacities of MG. The granules of group 2 which are characterized by higher adsorbed amounts of MG compared to the other groups are characterized by a high porosity and a larger grain size. They also show also an important adsorption amount of MG but still less than that of porous granules confirming the positive influence of the granule porosity on adsorption properties.

Group 3 includes bentonite formulations treated with iron alone, in the presence of CTAB, in the presence of gluten, and gluten alone as well as activated carbon. These adsorbents are characterized by low porosity and particle size. Group 3 includes bentonite formulations treated with iron alone, in the presence of CTAB, in the presence of gluten, and gluten alone as well as activated carbon. These adsorbents are characterized by low porosity and low grain size. This group is characterized by the highest pHzpc and SSA values.

According to all these results, it appears clearly that samples of each group seem to share the same properties.

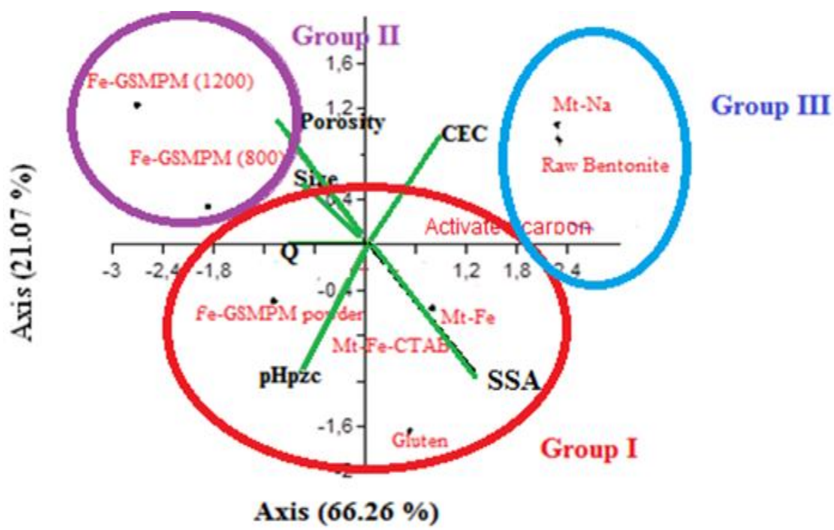

Fig. 4. Projection of the parameters studied at the individual level (axis 1-2).

The successive stages carried out by the PCA method make it possible, in the last step, to obtain an explanatory factor map of the different correlations between the studied parameters. The corresponding results make it possible to carry out a first typological analysis of these different variables according to their individual affinities, as well as to determine their contributions to the first two principal components.

The final exploitation of all these results from the factorial map therefore allows us to draw the following conclusions:

• The size and porosity of the Fe-GSMPM granules simultaneously influence their adsorptive properties of the MG dye.

• The pHzpc does not seem to be affected by the size and porosity of the granules.

The statistical analysis, carried out by the principal component analysis (PCA) method, allowed to correlate well the structural properties in terms of size, porosity SAA and pHzpc with those of the adsorption of the solute used with percentage inertia of 66 %.

4. Conclusion

In this study, a laboratory investigation was carried out to prepare coherent and consistent adsorbent granules noted Fe-SMPMG based on powders of an iron surfactant modified pillared montmorillonite (Fe-SMPM) and gluten as an inert binder.

These new granulated sorbents have been found to be very effective in removing the malachite green dye MG from aqueous solutions. Here, the statistical tool of the analysis in primary components (PCA) is used in order to have a more precise idea of the existing links between the data (variables and responses). The PCA confirms the existence of significant correlations between the size, the porosity, the SSA and the pHzpc with the quantity of adsorption Q of the granules of Fe-GSMPM. In particular, the existence of a significant correlation between the size of the granules and Q, suggests that there is a strong affinity between these two parameters. These correlations suggest that the size and porosity of these granules strongly influence the amounts of dyes adsorbed.

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