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Purification of pigment contaminated wastewater by the adsorption method in the textile industry

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Abstract

The activities of societies are increasingly seriously affecting the reproduction of living environments: soil, air, surface and underground waters, forests, rivers, lakes, seas and oceans, Greenhouse effect and damage to the ozone layer [1,2]. The textile industry uses toxic synthetic dyes which pollute its waste water.

The purpose of this research is in the context of the choice of an effective, local and cheap adsorbent for removing dyes from the waste water of the textile industry. The aim of this work is to exploit a mixture of seawater and bentonite. Sea water contains a large amount of magnesium and calcium salts. During the alkalization of one liter of sea water to pH ~ 11, 33 g of a mixture of $Mg(OH)_2$ and $(MgOH)_2 CO_3$ and ~ 1 g /l from $CaCO_3$. The previous work has shown that the hydroxides and basic salts of the carbonates of certain metals are more efficient adsorbents. [3,4,5].

Keywords: Sea water, bentonite, organic dyestuffs, adsorption, desorption and adsorption isotherm.

Introduction.

The increased use of organic dyes during dyeing to ensure proper impregnation of the latter on the fabric has rendered the water rejected by the textile industry polluted. Traditional processes do not elicit them almost entirely. This situation pushes us further to find efficient, available and less costly adsorbents. Analysis of sea water showed that 1 liter of sea water contains 0.409 g/l of calcium and 13.376 g/l of magnesium which can form at pH ~ 11 more than 30 g $Mg(OH)_2$.

Adsorption isotherms have shown that adsorption can be regulated by Langmuir and Freundlich isotherms. From the values of the maximum adsorption capacities and equilibrium constants, the mixing of seawater and bentonite is efficient adsorbent. This mixture can be used for purifying the water of the textile industry.

1. Part experience

In our previous work we obtained a good results when using a mixture of bentonite and $Mg(OH)_2$ obtained from magnesite.

Experience has shown that to purify litre of water polluted by acidic, direct and dispersive synthetic organic dyes with a concentration of 40 mg/l, it is sufficient to use ~ 20-25 ml of sea water. The kinetic study has shown that the adsorption process of acidic direct dyes and dispersants are adsorbed 95 - 100% in less than 10 minutes. Since the synthetic organic dyes are tensile-active and the particles of the adsorbents do not rush and remain in the water purify in dispersed (colloidal) form or flotation of the particles. This process is most intensive if the liquid to be purified contains additives.

To stop this process we used a necessary amount of activated active bentonite of "trioctaedric" layer having negative charges. Bentonite causes rapid coagulation of the dispersed particles of the adsorbent and also adsorbs dyes (synergistic effect).

Adsorption isotherms have shown that adsorption can be regulated by Langmuir and Freundlich isotherms. From the values of the maximum adsorption capacities and equilibrium constants, the mixing of seawater and bentonite is an efficient adsorbent. In this essential part

of our work we have developed the formulation of the dyes mentioned above by a mixture of mother and bentonite water which is summarized as follows:

1. Preparation of organic dye solutions with concentration by 0,02%.
2. Introduction to these solutions a definite quantity of seawater and different quantities of bentonite.
3. Maintenance of basic pH by using NaOH and Na₂CO₃ solutions.
4. Agitation of the mixture for a few minutes and determination of the time of clarifying the liquid obtained.
5. Separation of the liquid phase by decantation or filtration.
6. Analysis of the liquid phase.

2. Fixing of the various synthetic dyes with a mixture (Mg(OH)₂, (MgOH)₂ CO₃ and CaCO₃) obtained from seawater and bentonite.

In a series of 50 ml specimens numbered from 1 to 4, 10,00 ml of a concentrated solution of 0,02% dye are introduced. 0,2 ml of a solution containing 1 mole / l of NaOH and Na₂CO₃ (the pH of the liquid must be pH ~ 11) and various amounts (10, 20, 30, 40 mg) of bentonite. The volume of the solution is then adjusted to the specimen line by means of distilled water.

The adsorbed quantity of the dyes by mixtures: Mg(OH)₂, (MgOH)₂CO₃, CaCO₃ obtained from seawater and bentonite can be calculated according to the following formula:

$$\alpha = \frac{[C_0] - [C_e]}{[C_0]} \times 100\%$$

α : is the degree of adsorption in%; C_0 : the initial dye concentration; C_e : this is the concentration of colorant dye.

The equilibrium dye concentration is determined from the calibration curves that have been plotted for each dye.

Table 1.

Degree of adsorption in % of the various dyes with the mixture obtained (Mg(OH)₂, (MgOH)₂ CO₃ and CaCO₃) from seawater and bentonite

Colorants	Dyes the amount of bentonite in mg			
	10	20	30	40
	The volume taken from the sea water is 1.0 ml			
	Purifying in%			
Blue cibacet	73.5	81.5	87.20	92.5
Orange ceylon GR	70.5	76.40	82.5	93.3
Yellow KMP	73.5	78.4	85.45	94.30
Red suprantine F3B	75.30	84.20	89.55	96.2
Brown solophonyl-BCLE	76.20	86.24	94.50	98.52
Red erionyle	78.55	87.50	95.85	99.25
Blue K	79.25	88.50	96.20	99.70

The obtained results show that by use 1.0 ml of sea water and 40 mg of bentonite the purification is increased from 92.5 up to 99.7% (the contact time is 15 minutes).

3. Comparative Study with activated carbon

Activated carbon is certainly the most used element as an adsorbent. This is true at least for five reasons: Its good adsorption characteristics, its cost is relatively low, its availability, a wide use.

For all these reasons, we have therefore carried out comparative tests of the adsorbent studied (a mixture of seawater and bentonite) in our research with activated carbon. The activated charcoal powder used is Chemviron Filtrisorb - 400 of animal origin. It remains one of the most used coals in the treatment of water.

3.1. Determination of contact time with activated carbon.

The mass of the absorbent is 0.08 g for an initial dye concentration of 40 mg/l.

Table 2.

Absorbance of dyes as a function of stirring time in the presence of activated charcoal

Time	Absorbance						
In min	Blue Cibacet F3R	Orange Ceylon GR	Yellow KMP	Red Suprantine F3D	Brown Solophenyl BGLE	Red erionyle	Blue K
0	0.385	0.570	0.479	1.145	0.905	0.890	0.515
30	0.259	0.326	0.295	1.105	0.755	0.525	0.305
60	0.175	0.295	0.265	0.955	0.605	0.385	0.270
90	0.145	0.267	0.215	0.905	0.428	0.345	0.230
120	0.122	0.245	0.165	0.795	0.375	0.315	0.195
150	0.120	0.243	0.165	0.790	0.373	0.315	0.190
180	0.120	0.243	0.165	0.790	0.373	0.315	0.190

The adsorption kinetics of the activated carbon make it possible to determine the optimum stirring times for each dye. This time is estimated at 2 hours. While the optimum stirring times for each dye in the use of our adsorbent (seawater products in the presence of bentonite) are evaluated at 10-15 minutes.

3.2. Solvent adsorption on activated carbon.

The adsorption isotherm is traced at a temperature of 24°C, under the following conditions:

- The contact time for all dyes is 120 min.
- The agitation speed is 200 rounds / minute.
- The volume of the solution is 50 ml.
- The initial concentration of dye is 40mg/l.
- The adsorbent masses are in the range of ~0.01 to ~0.075 g.

After stirring for 120 minutes, the mixture is centrifuged or filtered. The absorbances of the clear filtrates will inform about the residual concentrations of dyes (concentration in equilibrium).

The quantities of dyes (in mg) adsorbed per 1 g of adsorbent are calculated

By the following formula:

$$Q_{\text{exp}} = (C_0 - C_e) / 20.M$$

C₀: initial concentration in mg /l.

C_e: concentration at equilibrium in mg /l

M: mass of the adsorbent in g.

The percentage of purification is calculated by the following formula:

% Purification = (C₀ - C_e). 100/C₀.

The results of the calculations are grouped in the following tables. The results of the adsorption of the textile dyes on the activated carbon made it possible to compare the efficiency of formation on the two adsorbents. This comparison is presented in table 3.

Table 3.

The efficacy of fixing the dyes on the same amount of two adsorbents

The adsorbents Mass of adsorbent Colorants	Carbon active 0.075 g	The product of sea water and bentonite 0.075
Blue cibacet F3R	73.75	92.5
Orange ceylon GR	66.20	93.3
Yellow KMP	58.75	94.30
Red suprantine F3B	67.20	96.2
Brown solophenyl-BCLE	68.52	98.52
Red erionyle	62.58	99.5
Blue K	59.50	99.70

Note: We have indicated that sea water contains 0.41 g/l of calcium and 13.376 g /l of magnesium, so each ml of sea water can give ~ 0.00 lg of CaCO_3 and ~ 0.0325 g Of $\text{Mg}(\text{OH})_2$ and the total amount of the adsorbent in 1 ml of the sea water will be equal to $0.001 + 0.0325 = \sim 0.0335$ g of $\text{Mg}(\text{OH})_2$ and CaCO_3 .

Proceeding from that if the added amounts of bentonite (10, 20, 30, 40 mg) are introduced there will be different amounts of the adsorbents: ~ 0.043 ; 0.053 ; 0.063 ; 0.073 . Our experiments were conducted under identical conditions, namely, the same initial concentration of dye, and the same mass of our adsorbent and activated carbon. For the same mass of 0.075 g of adsorbent and activated carbon, their degrees of purification are distinctly different. Indeed, activated carbon purified from 58.75 to 73.75% while the purified adsorbent was purified from 92.5 to 99.70%.

4. Desorption tests

The dyes are rather adsorbed on the active sludge than biodegraded by it. This is confirmed by the fact that the reject sludges are generally dyed, so the dyes can exist in the sludge.

The presence of the dyes in the sludge poses the following problem: is the phenomenon of dyeing the dyes by the sludge reversible? In other words, is there a release of dyes, in case of rain or other conditions?

In our research, we considered this risk of release. For this purpose, a number of experiments have been carried out to ensure a good dyeing of the dyes by the adsorbent which we propose.

The desorption tests of the various dyes tested were carried out as follows: A mass of 0.45 g of adsorbent in 100 ml of distilled water containing the dye at a concentration of 0.2 g / l was stirred for 2 hours. After centrifugation, the adsorbent was dried at 105°C . until the constant weight was obtained.

After cooling, a mass of 0.0560 g of adsorbent is brought into contact with distilled water (100 ml). After stirring for 3 hours, the absorbance is centrifuged and absorbed to determine the amount of dye absorbed in the distilled water.

Table 4.

Desorption of dyes

Colorants	m_0/mg	m_1/mg	Desorbition %/
Blue cibacet F3R	0.58	0.025	1.45
Orange ceylon GR	0.62	0.032	1.9
Yellow KMP	0.65	0.047	3.0
Red suprantine F3B	0.77	0.055	4.2
Brown solophenyl-BCLE	0.82	0.062	5.08
Red erionyle	0.85	0.077	6.54
Blue K	0.92	0.088	8.09

m_0 : adsorbed dye mass; m_1 : mass of dye desorbed

The percentage of desorption is calculated as follows: Desorption in % = $(m_0/m_1) \cdot 100\%$ (table 4). Recapitulates the desorption percentages of the various dyes. These values are at least 1.45% and at most 8.09% desorption. This proves that these dyes are well fixed by the adsorbent proposed in our research study. Even if the release phenomenon existed, it would have no effect on the environment because the dyes are well fixed on the adsorbent on the one hand. On the other hand, the percentage of desorption is very low.

5. Industrial application

All the applications we have seen up to now are on a laboratory scale. The tests were carried out on synthetically polluted waters.

At this level of our research, it becomes necessary to carry out experiments on an industrial effluent.

In an industrial sample, waste water containing the various dyestuffs was used for the determination of BOD_5 (Biochemical Oxygen Demand) for oxygen consumption five days

(mg O₂ /l), Conditions of the test (dark and at 20°C), results of the metabolisation of organic pollution biodegradable by microorganisms of banal contamination of the waters. OCD (oxygen chemical demand): oxygen consumption (in mg O₂/l) under the conditions of an oxidation reaction by potassium dichromate in sulfuric acid medium, in the presence of heat, a catalyst. These parameters provide information on the degree of pollution of these discharge waters.

A mass $m = 0.75$ g of adsorbent was introduced into a volume of 500 ml of waste water. This water is filtered on a sintered glass filter 4. The results of the pollution parameters are given in table 5.

Table 5.

DBO5 and DCO before and after treatment of an industrial influent

	BOD5 en mg/l		OCD en mg/l	
	Water effluent	Standard	Water effluent	Standard
Before treatment	220	40	1080	120
After treatment	10		54	

Two main findings emerge from this table:

-The industrial effluent is very polluting and the BOD₅ and OCD parameters are clearly above the required standards.

The treatment we propose is effective and cheap (as an adsorbent is seawater and local bentonite). The developed adsorbent concentrates the pollutants by decreasing BOD₅ and OCD. This decrease is of the order of 95%. The obtained results are very convincing and the values of the BOD₅ and OCD parameters are considerably lower than the norms.

6. Regeneration of adsorbents

On the industrial scale, the treatment of wastewater from textiles generates huge amounts of sludge containing a high levels of dyes. These dyes adsorbed by these active sludges are only biodegradable by this. This is confirmed by the fact that these reject sludges are generally dyed. The presence of dyes in these sludges is a major problem.

We have considered for a complete treatment and treatment without any short-term or long-term disadvantage, we have considered the regeneration (recycling) of these adsorbents by the following reasons:

1. Recovery of the adsorbents for an earlier reuse which will make the treatment of water rejected by the textile units less expensive.

2. Avoid the accumulation of sludge, which will take up more space and which allowed us to elaborate the general experimental protocols that we propose hereafter. 6.1. Proposed method of sludge regeneration.

The sludge obtained using the mixture composed of: active natural bentonite; Mg(OH)₂ (MgOH)₂CO₃, CaCO₃ obtained from sea water and adsorbed organic dyestuffs.

1. Calcination of the sludge at 400 - 500 ° C, according to the literature, at this time interval the structure of the bentonite remains unchanged. There will be only the elimination of the costs organic (dyes) and decomposition of Mg (OH)₂ (MgOH)₂CO₃, CaCO₃ to oxide of metals MgO, CaO.

2. Treatment of the remaining mass with a dilute solution of HCl (1:3): MgO + CaO + bentonite + 4HCl MgCl₂ + CaCl₂ + bentonite + H₂O Note: Bentonite does not dissolve in HCl solution.

3. Treatment products by a mixture of solutions:

NaOH, Na₂CO₃ + NaOH, Na₂CO₃, MgCl₂ + CaCl₂, Mg(OH)₂ + Mg(OH)₂CO₃ + CaCO₃

Note: Bentonite remains unchanged.

Thus the mixture of adsorbents which can be used for the purification of water contaminated with organic dyes is again obtained.

It should be noted that the implementation of this regeneration technique is simple and does not require enormous investment from the company.

7. Enrollment of the proposed treatment scheme.

The quantities of dyes and additives remaining in the baths after dyeing leave with the finishing waters. Among the operations involved in the filling is washing, which allows the extraction of non-fixed dyes by the fibers using detergents. This means that the finishing waters contain large quantities of pollutants (organic dyes, additives, detergents, textile material, etc.) and are sent to the treatment plant.

Conclusion:

The degree of adsorption in% of the various dyes was determined with the resulting mixture $(\text{Mg}(\text{OH})_2)$, $(\text{MgOH})_2\text{CO}_3$ and CaCO_3 from seawater and bentonite.

The results obtained show that, when using 1.0 ml of sea water and 40 mg of bentonite, the purification passes from 93 to 99%.

Comparative tests of the adsorbent studied (a mixture of sea water and bentonite) were carried out in our research with activated charcoal. The activated carbon purified from 58.75 to 73.75% while the purified adsorbent was purified from 92.5 to 99.70%. Purification tests were carried out on an industrial sample, constituting reject water containing the various dyes. The treatment we propose is effective and cheap (as adsorbent is seawater and local bentonite). Indeed, the adsorbent developed fixes the pollutants by decreasing the BOD5 and COD. This decrease is of the order of 95%. The results obtained are very convincing and the values of the BOD5 and COD parameters are considerably lower than the norms.

A technique has been proposed for regenerating formed sludge. This regeneration technique is simple and does not require enormous investment on the part of the company.

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