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EVALUATION OF THE EFFICIENCY OF CONTACT COAGULATION IN THE TREATMENT OF WASTE WATER

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HODNOTENIE EFEKTÍVNOSTI KONTAKTNEJ KOAGULÁCIE PRI ČISTENÍ ODPODOVEJ VODY

ABSTRACT
The objective of this paper is to study the possibility of treating waste water with activated clay and with an activated mixture of clay and an industrial powder which induces coagulation. Coagulation resulting from physical contact, i.e. from the collision between soft particles of aggregation of the colloidal suspension in water and hard rigid granules of various powders is called contact coagulation. It is unlike classical or volume coagulation which result from mixing the soft particles from the wastes with hydrolyzed Al and Fe salts. Contact coagulation is illustrated by the results obtained from treatment of the waste water released from a slaughter house and a dairy, by the coagulation with the activated clay mixture and pulverisation from fumes released from the steel production furnaces. A strong anion flocculant was used for flocculation.A decrease of COD in the treated water from the slaughter house ranged from 75-89%, and in the waste water released from the dairy from 54-82%. The advantages of contact coagulation and the possibility of using various industrial waste by-products with a good ability of absorption for waste water treatment are pointed out in this paper.
Key words: *waste water, waste water treatment; volume and contact coagulation; flocculation; clay; ferric powder*

INTRODUCTION

Coagulation-flocculation and settlement by using ferric and aluminium salts is the most common procedure in industrial waste water treatment, particularly in pre-treatment (Ramley *et al.*, 1981;O' Melia, 1985). This primarily refers to waste water containing toxic substances, e.g. waste water released by the textile and leather industries (and similar industries) as well as for waste water containig fats/oils (dairies, oil production), since an extremely high content of fats can block biological processes.

This procedure can be used as a final treatment, particularly by small plants which do not work effectively continuously and are located outside the cities and, therefore, are not connected to the city sewer system, i.e. to the city biological treatment plant.

However, it is often not possible to carry out efficient coagulation-flocculation by means of the mentioned metallic salts with the addition of organic flocculants, especially if the waste water contains mainly organic substances.

Coagulation

Colloid and finely dispersed systems have a certain anticoagulation stability due to a moisturising coating and double electrical field around the particles. This anticoagulation stability can be disturbed in various ways; heating, freezing, addition of electrolytes and application of an electrical field.

It is well-known that the water ingredients can be either hydrophilic or hydrophobic. Hydrophilic ingredients, which mainly consist of organic dispersions, have a significant water quantity in their moisturising coating due to the presence of the so-called polar groups-OH,- COOH. Due to a weak electrical charge and large moisturising coating, the hydrophilic particles do not easily coagulate.

Hydrophobic particles, such as clay, silt, etc., have hardly any moisturising coating, they have a strong electrical charge and easily coagulate. They usually have a crystalloid structure with a large surface and can absorb various substances from the water and thus become electrically charged.

In a natural environment the particles are most frequently negatively charged. Due to the exertion of electrostatic forces and diffusion forces two layers are formed on the surface of the particles, i.e. a fixed bounded absorption layer and a mobile diffusion layer. While the particles move in the solution, the core potential is partly neutralised in the absorption and partly in the mobile diffusion layer. The difference between the potentials of the fixed absorption layer and mobile diffusion layers is referred to as elektrokinetic or zeta potential and it represents the degree to which the colloid particles can approach each other (Voznaj, 1981; Nikoladze, 1989; Koganovski, 1983; Kemmer, 1979).

The main purpose of coagulation is the destabilisation of colloid systems which results in the neutralisation of the zeta potential, i.e. which enables the particles to form aggregate-flocs.

In natural hydrophobic colloids the zeta potential is reduced below 30 mV. By adding electrolytes an isoelectric state is formed at the so-called isoelectric point which ranges between 6.5 and 7.5 pH values in most colloids. At the medium pH value, the layer of the moisturising coating among the particles and the charge are the lowest.

The electrolytes used as coagulants are ferric and aluminium salts, i.e. most frequently $FeCl_3$ (Ching *et al.*, 1994) and $Al_2(SO_4)_3$ (Edzwald, 1993;Van Benschoten &Edzwald, 1990). These salts react with water by forming hydrates, i.e. hydrocomplexes which are easily polymerised and act as absorbents and neutralise the electrical charge which results in coagulation and settlement of waste matter from the water (McCurdy *et al.,* 2004; Metcalf-Eddy, 1980).

Coagulation is a complex process with three main effects: coagulation-flocculation, co-precipitation and absorption. When aggregates are formed by coagulation two phases can be distinguished: perikinetic and ortokinetic. In the perikinetic phase the zeta potential is neutralised and small aggregates are formed which cannot move by the action of the Brown thermic circulation. This perikinetic phase is short, lasting only a few seconds. It then passes into the so-called ortokinetic phase in which larger aggregates are gradually formed. In order to initiate a faster and more direct contact between the particles, they should be mixed. At the beginning, this mixing is rapid so that a better dispersion of coagulants in the entire volume can be obtained. After 1-2 minutes the mixing is slow, so that the growth of the flocs can be increased to a maximum as fast as possible and their destruction can be prevented.

Contact coagulation

The coagulation process, due to the effect of Fe and Al salts, occurs between particles of approximately the same dispersion state, i.e. between the soft particles when the coagulation is referred to as volume. This distinguishes it from contact coagulation resulting from the contact-collision between the soft particles in the water and the hard particles of hydrophobic colloids.

If drinking water is filtered, and a small quantity of inorganic coagulants is added to turbid water, it can be noted that instantaneous coagulation occurs at the contact between the turbidity particles with the granules of the filtration sand layer which greatly facilitates the filtration process (Desjardins *et al.*, 2002).

Waste matter from water is usually slightly charged and can be more easily bounded to large hard particles which are not charged than to the same particles of the waste matter.

The process of contact coagulation is characterised by a more efficient treatment and smaller consumption of coagulants. This can be explained by the fact that better contact is obtained between the hard granules and wastes from the water than between soft coagulant particles and wastes (as in volume coagulation).

MATERIALS AND METHODS

Coagulation-floculation was performed by a jar-test technique so that 1000 mg/L of coagulants were added to 200 mL of waste water and subsequently 2 mg/L of flocculants. After mixing 10 minutes at an initial rapid mixing of 120 r/min and a subsequent slow mixing at 40 r/min the water was allowed to settle (30 min) and pH, COD, total N, total P, metals and transparency (%) were determined in the supernatant. Measurements of pH were taken with a pHmeter, chemical oxygen demand (COD) was determined according to American Standard Methods (APHA,WPCF, 1995). Total N was determined using fenol-hypoclorite after Kjeldhal burning (Scheiner, 1976) and total P was determined using ammonium molibdate with the reduction by ascorbic acid after boiling with acids and oxidation with persulphate (Murphy & Riley, 1966). The metals were determined by atomic absorption. Transparency (%) was determined on the spectrofotometer at a wavelength of 540 nm.

The coagulant was prepared by using the ferric powder from the cyclone of the emissions released from the furnaces of the steel production plant in Kaštel Sućurac near Split (Croatia).

The waste ferric powder usually contains the following ingredients: 60% Fe_2O_3, 15 % CaO , 3.5% MgO, 5% SiO_2, 4.5 % , MnO.

Calcium, magnesium and silicium compounds mainly originate from the mantle-lining of the electrical furnace and the other compounds generally originate from the iron coatings, galvanium layers and other metals which are melted together with iron.

A flocculant Nalco SC 667 which appears on the market as a 30% oil suspension (Lemkuhl & Pressleim, 1990) was used in the waste water treatment.

RESULTS AND DISCUSSION

In order to apply contact coagulation in the treatment of waste water a 20% water suspension of coagulants was prepared and the metal content was analysed in the soluble part (supernatant). The results are presented in Table 1. This coagulant was used for the treatment, i.e. coagulation-flocculation of the waste water from the slaughter house by a jar-test, so that 1000 mg/L of coagulants were added as well as 2 mL of flocculants; they were mixed for 10 minutes.The metal content was analyzed in the treated water after settlement. The results are presented in Table 2. Tables 1 and 2 show that the coagulant, as well as the treated water, contains the greatest quantity of zinc, followed by manganese and the smallest quantity of iron. Zinc and manganese, found in the soluble part of the coagulant, are necessary for coagulation and have the same effect as Al and Fe salts.

A low iron content in the coagulant and treated water can be explained by the fact that iron oxides, when exposed to a high temperature in the electric-arch furnace, become insoluble in acids. The cadmium and lead contents are also low in waste water and after dilution in the recipient do not present an environmental threat.

Since the soluble toxic metals are present in the coagulant, i.e. in the effluent after treatment, the justifiability of that coagulant from the ecological aspect becomes questionable. The soluble alloys content should be reduced so that the metal concentration in the effluent satisfies certain standards. Since Croatia does not have standards for the effluent quality, MAC values of some metals are mentioned in the water used for irrigation according to FAO (Kos, 1991). According to those recommendations the MAC values are as follows:

Zinc	2	mg/L
Manganese	0.2	mg/L
Iron	5	mg/L
Cadmium	0.01	mg/L
Copper	0.2	mg/L

The strictest criterion refers to the cadmium content because it is easily accumulated in soil and plants in a concentration which can be hazardous to humans.

Since this coagulant is very efficient and economical, in order to make it ecologically acceptable, the quantity of soluble metals was reduced to 75%. Thus, it was possible to perform the coagulation with a coagulant containing 240 mg/L Zn and 60 mg/L Mn. In three samples the following was found:

4.5; 3.8; 1.8 mg/L Zn
0.65; 0.34; 0.46 mg/L Mn

The coagulant can also be prepared by using pure raw materials, but in that case it is necessary to add small quantities of Al and Fe salts.

Hence, efficient coagulation was performed by also adding, apart from this coagulant, 25 mg/L $FeCl_3$ x$6H_2O$ to the waste water.

The coagulant can also be prepared with clay without the addition of the ferric powder. It has the same coagulation properties but it is a worse absorbent as it does not absorb the colour of blood from water released from the slaughter house.

However, this coagulant does not have any negative effects upon the environment and is therefore acceptable from the ecological point of view; hence, it is an optimal solution for obtaining silt for composting or for obtaining treated water for agricultural irrigation. This approach to the solution of waste water problems has become more acute in recent years (Kos, 1991).

It should be stressed that each type of waste water has its own characteristics so that the respective content and quantity of coagulants should be determined by analysing each water type. The analyses of the treatment efficiency were performed on waste water samples from the dairy and slaughter house.

The samples from the Salonacoop slaughter house in Vranjic near Split were usually taken after slaughter. The slaughter house works in the morning for 3-4 hours and has a basin for egalization and equipment for mechanically treating larger ingredients. This water has a slightly red blood colour. Most of the blood is collected in containers and is not released as waste water (Štambuk-Giljanović, 2006). The coagulation in this waste water was performed by a mixture of clay and ferric powder with the addition of flocculants. The results of the analyses are presented in Table 3.

The samples of waste water from the dairy were taken from a manhole where the waste water from the city dairy is collected before it is released into the sewer system. The samples were taken once and the treatment was performed in the same way as for the water from the slaughter house. The results are presented in Table 4. The Table also presents the results obtained after the treatment of nine average, composite, 2-hour samples treated by coagulation by clay (Štambuk-Giljanović, 2002).

The best indicators of waste water treatment efficiency are as follows: pH, transparency (%), chemical oxygen demand (COD), total N and total P. BOD_5 was not considered since this analysis would take five days and, therefore, is not suitable for a daily routine control. In addition, there is a certain ratio between BOD_5 and COD for each waste water type, so that after the determination of that ratio it is not necessary to determine BOD_5.

It is evident from the results that the transparency in all samples of treated water was high which shows that the suspended matter was completely removed. A relative decrease of COD in the treated water from the slaughter house ranged from 75-89%, and in the waste water released from the dairy from 54-82%. This decrease was higher in waste water with higher COD, and it is generally higher in waste water from the slaughter house than from the dairy. This could be expected since the waste water from the dairy contains ingredients which are not so easily absorbed such as sugar, organic acids, esters, etc.

If different quantities of coagulants are added to waste water, there is a certain small, i. e. optimal quantity of coagulants at which the coagulation process occurs.The addition of greater coagulant quantities, beyond the optimal ones, would be inefficient from the technological and economic aspects. However, the addition of flocculants can result in a decrease in the optimal quantity of coagulants. Furthermore, the coagulation process is accelerated and the effluent flocs and transparency are increased. It was found that the optimal quantity of the described contact coagulants (with a particle size up to 0.5 mm) ranges from 400-1200 mg/L with the addition of flocculants while it should range from 2-4 g/L without the addition of flocculants. Organic flocculants are polymerised organic electrolytes most often based on polyamides-polyakrilamides or polyamides. Anion flocculants, which are added after the coagulants during rapid mixing, are usually used for the treatment of waste water of organic origin. Flocculants are produced as 100% granulated powder or as 30% oil suspension. They are added to the waste water as diluted viscous solutions (0.02-0.1 per cent), usually in quantities from 1-10 mg/L.

The classical volume coagulation by using Al and Fe salts as coagulants has certain disadvantages, such as:

- high consumption of Al and Fe salts, especially if the treated water has a high organic matter content,
- flocs of small density are formed which slowly settle and form a large mass,
- the procedure is quite sensitive to changes in pH, temperature, changes in the waste water state and to doses of coagulants.

By using contact coagulants the mentioned disadvantages can be reduced or completely eliminated.

Various raw materials can be used for the preparation of coagulants for contact coagulation. Thus, one of the coagulants which can be used is a mixture of clay and ferric powder which should be treated by mineral acids. This coagulant is used as 10% or 20% water suspension.

Contact coagulation has significant advantages when compared to classic coagulation such as:

- the coagulation process and, particularly, settling are more rapid than in classical coagulation;
- sensitivity to the influence of pH and temperature are lower if pH in the water is within allowable limits from 6.5-9, the pH value need not be corrected;
- colour removal is more efficient.
- unlikely error due to coagulant overdose.

On the other hand, in classical coagulation, the addition of excessive quantities of Al and Fe salts leads to the restitution of the settled particles into the suspension, therefore the treatment effects are improved:

- more efficient clearing and higher transparency of the treated water;
- smaller volume of the settled matter (up to 50%);
- relatively simple and inexpensive production of coagulants;
- simple operation of the treatment plant.

This paper presents several examples of treating two different types of waste water in order to stress the possibility of efficient treatment by using contact coagulation since that process has significant technological advantages over the classical method. The application of contact coagulation to waste water treatment can be considered to be an innovative approach to waste water treatment by coagulation.

CONCLUSIONS

This paper considers the possibility of waste water treatment by using physical-chemical processes of coagulation-flocculation-settling by means of solid insoluble inorganic coagulants. Since during this process coagulation initially results from the reaction of soluble salts and subsequently by the contact between solid coagulant particles and soft particles of the waste water constituents, this process is applied in the filtration of drinking water. The same principle is used for waste water treatment. This paper presents coagulants based on a mixture of clay and ferric powder as well as coagulants based only on clay.

Transparency in all samples of the treated waste water was high (54-87.8%). The decrease of COD in the treated water from the slaughter house ranged from 75 - 89% and in the waste water released from the dairy from 54-82%.

Contact coagulation requires a larger quantity of coagulants (ca 1 g/L). However, these coagulants mainly consist of natural and waste raw materials and are easily prepared. Raw material for the coagulants production can contain ingredients, primarily metals, which can have hazardous effects upon the environment. This paper deals with the possibility of removing these constituents.

List of Tables

Table 1. Metal content in the soluble part of coagulants

Metal, mg/L	Zn	Mn	Fe	Cd	Pb
Coagulant 1	487	660	0.17	8.7	9.8
Coagulant 2	846	447	0.12	4.8	5.2
Cogulant 3	890	604	0.09	3.6	2.8
Coagulant 4	973	55	0.02	4.8	6.4
Coagulant 5	980	80	0.07	1.2	2.6

Table 2. Metal content in treated waste water

Metal, mg/L	Zn	Mn	Fe	Cd	Pb
Treated water+coagulant 2	42	7	0.010	0.47	0.5
Treated water+coagulant 3	63	18	0.003	0.12	0.02
Treated water+coagulant 4	24	5	0.007	0.18	0.04

Table 3. Results of waste water from the slaughter house analyses before and after treatment by a mixture of clay and ferric powder with the addition of flocculants

Parameters	slaughter house							
	waste water	treated water		waste water	treated water		waste water	treated water
		1[a]	2[b]		1[a]	2[b]		
pH	9.5	9.2	7.3	7.4	7.1	7.3	7.8	7.0
COD, mgO_2/L	950	210	230	1.420	172	158	293	82
Efficiency,%	-	77.8	75.8	-	87.8	88.9	-	72
Total N, mg N/L	84	31	30	120	25	22	32	7
Total P, mgP/L	6.3	0.78	0.47	7.3	0.7	1.1	3.2	0.4

Transparency, %	1.4	98	99	19	98	93	45	92

1[a] - coagulant 1
2 [b] - coagulant 2

Table 4. Results of waste water from the dairy analyses before and after treatment by a mixture of clay and ferric powder with the addition of flocculants

Parameters	dairy							
	waste water	treated water		waste water	treated water		waste water*	treated water
		1[a]	2[b]		1[a]	2		
pH	8.07	8.6	8.2	8.1	7.6	7.4	6.2	8.3
COD, mgO_2/L	610	260	280	910	270	250	1750	312
Efficiency,%	-	57.4	54.1	-	70.3	72.5	-	82.2
Total N, mg N/L	53	19	21	58	24	27	22.3	8.6
Total P, mgP/L	2.8	0.53	0.74	19	0.30	0.32	4.2	0.07
Transparency, %	63	90	93	26	92	95	3.7	96

1[a] - coagulant 1
2 [b] - coagulant 2
* nine average composite, 2 hour samples treated by coagulation by clay

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