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DOLOMITE COAGULATION-ADSORPTION: A NEW TECHNOLOGY FOR WATER TREATMENT

The principles and the parameters of a novel water treatment technology, in which processed dolomite is used as coagulant, are presented. The technology has been developed by making use of the results obtained from laboratory scale experiments on model solutions and a variety of natural water samples. The parameters of the coagulant obtained from raw dolomite have been determined by investigating its thermal dissociation and hydration.

Treatment effects are assessed in terms of coloured-matter, turbidity, TOC and COD removal. The technology is successful when applied to the treatment of surface water irrespective of the pollution level. The effluent is clear and colourless, displaying a high removal of organic matter and heavy metals, as well as a partial inactivation of viruses and bacteria. Following a single-stage recarbonation process, water treated via the technology of interest exerts no corrosive action.

The optimum dolomite coagulant dose depends exclusively on the influent alkalinity provided that turbidity level and coloured matter concentration are moderately high. The optimum pH for the treatment process approaches 10.5.

The technology is an advantageous combination of three unit processes – decarbonation, coagulation and adsorption.

1. INTRODUCTION

Physicochemical methods are still widely used in water treatment. Of these, coagulation and adsorption have always received considerable popularity for yielding high removal efficiencies. These days, both the methods are coming into general use, because the pollution level in surface waters shows a tendency to increase. Besides alum coagulation, it is also the lime-magnesium coagulation process that is beginning to become a common practice.

During the past decades, a number of investigators concerned with water and wastewater treatment technologies involving alkaline media have directed their attention to the influence of calcium carbonate and magnesium hydroxide (both

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precipitated in lime coagulation) on the treatment effects. This influence, reported firstly in the late twenties [1], led to the following findings: 1) the lime dose applied affects the efficiency of clarifying surface water, and 2) the relationship between lime dosage and clarifying effects should be attributed to the properties of magnesium hydroxide precipitated from magnesium salts present in the water. Therefore, in a number of experimental studies the coagulating and adsorbing properties of magnesium hydroxide are used. These approaches yielded a water treatment method in which magnesium carbonate (precipitated as magnesium hydroxide in the presence of lime) acted as a coagulant [2], [3]. The investigations also revealed that magnesium hydroxide removed coloured matter as well as turbidity which is as high as that achieved with alum, and the suspended particles produced are even easier to settle. Experiments run on municipal sewage samples have supported the contribution of calcium carbonate and magnesium hydroxide to the removal of organics and phosphates [4]–[7].

Preliminary results from an earlier study accomplished by the authors of this paper showed that dolomite (a mineral containing calcium carbonate and magnesium carbonate occurring in abundance everywhere) was applicable as a source of lime and magnesium hydroxide [8]. Furthermore, the study revealed that a dolomite coagulant yielded a higher removal of pollutants from the treated water than lime and magnesium salts did. Taking these all into account, it may be concluded that the final effect of water treatment in an alkaline medium can be considered as a joint contribution of calcium carbonate and magnesium hydroxide particles influencing the pollutants present in the water.

2. MAIN IDEA OF THE TECHNOLOGY

The primary objective of lime coagulation involving magnesium salts (MgCO_3 , MgCl_2 , MgSO_4) as coagulants is a high alkalization of the water (pH level higher than 11.3) to accelerate the precipitation of magnesium hydroxide. The process, however, has two inherent limitations set by economic reasons — the high consumption of lime (specifically when the influent stream displays high alkalinity levels) and the overalkalization of the water under treatment, which requires a two-stage recarbonation in order to decrease the salinity level. There is one more disadvantage of applying lime coagulation — the complete disappearance of magnesium, an important microelement for an appropriate functioning of the human organism. The absence of magnesium creates favourable conditions for the incidence of many ailments associated with our civilization.

Taking the above into account the authors made an attempt to develop such a water treatment technology that would include all of the advantages inherent to the lime–magnesium treatment method without its limitations. It was, therefore, necessary to prepare a coagulant composed of both lime and magnesium hydroxide

in appropriate proportions so as to meet the requirements of an efficient water treatment. The data sets obtained from a number of preliminary investigations have substantiated the choice of dolomite, a mineral wherein calcium carbonate and magnesium carbonate account for 60% and 40%, respectively.

3. EXPERIMENTAL PROCEDURES

Unprocessed dolomite fails to comply with the conditions of the coagulation process. The objective of the initial stage of the study was to convert the mineral to a profitable form, i.e., to that of calcium hydroxide and magnesium hydroxide. Thus, dolomite samples of different types were subject to thermal dissociation in ambient air at 773 to 1173 K for 1 to 8 hours to achieve the oxide form. Hydration of the two oxides to calcium hydroxide and magnesium hydroxide was carried out at water-to-dolomite (dry weight) ratios varying from 1:1 to 5:1. To increase the degree of dispersion, magnesium hydroxide was peptized by the addition of magnesium chloride (at a proportion of 2 to 10 wt.% to the dry weight of the coagulant) to the slaking water. Thermal dissociation of dolomite was also investigated by the DTA method.

The second stage of the study involved water treatment by the jar-test method and by a semi-commercial through-flow model approach. The samples tested were model solutions or natural waters. The dolomite coagulant (in the form of 2% suspensions) was applied in doses ranging from 50 to 600 $\text{g}\cdot\text{m}^{-3}$. The jar-test was carried out at the following parameters: rapid mix ($G = 200\text{ s}^{-1}$), 2 minutes; flocculation ($G = 20\text{ s}^{-1}$), 20 minutes; settling, 30 minutes. The through-flow model consisted of a rapid mix tank ($G = 200\text{ s}^{-1}$, $t = 2\text{ min}$), a sludge-blanket clarifier, and a sand filter. Water flow velocity (vertical) in the sludge-blanket clarifier amounted to $2,5\text{ mm}\cdot\text{s}^{-1}$, filtration rate on the sand bed being $5\text{ m}\cdot\text{h}^{-1}$. Before filtration, the effluent was recarbonized with gaseous carbon dioxide to the pH of stabilization. Analyses were carried out by standard methods (colour, turbidity, alkalinity, pH, COD, Ca^{2+} , Mg^{2+}). The determination of total organic carbon involved a Beckman Analyser TOC.

4. RESULTS AND DISCUSSION

4.1. PREPARATION OF DOLOMITE COAGULANT

A typical chemical composition of the experimental dolomite is shown in tab. 1. The study of the thermal dissociation of raw dolomite has revealed that the process is primarily temperature-dependent and a function of time. The chemical composition of the dolomite also affects the course of the dissociation process. The adopted

Table 1

Chemical composition of the dolomite (all values are in wt.%)

Component	Raw dolomite	Decarbonized dolomite
CaCO ₃	54.50	—
CaO	—	61.50
MgCO ₃	30.60	—
MgO	—	26.80
Fe ₂ O ₃ +Al ₂ O ₃	2.61	3.72
SiO ₂	1.27	1.78
H ₂ O	1.02	—
Zn	0.005	0.006
Pb	0.001	0.001
Cu	0.001	0.001
Ni	0.000	0.000

criterion for the efficiency of thermal dissociation includes the achievement of limit mass loss at the lowest possible temperature and the shortest possible time. On assuming these, a complete conversion of calcium carbonate and magnesium carbonate to calcium oxide, magnesium oxide and carbon dioxide may be obtained without "overburning" of magnesium oxide, thus eliminating (or significantly inhibiting) its hydration. Figure 1 gives the thermogram of raw dolomite, and fig. 2 shows the kinetics of its thermal dissociation.

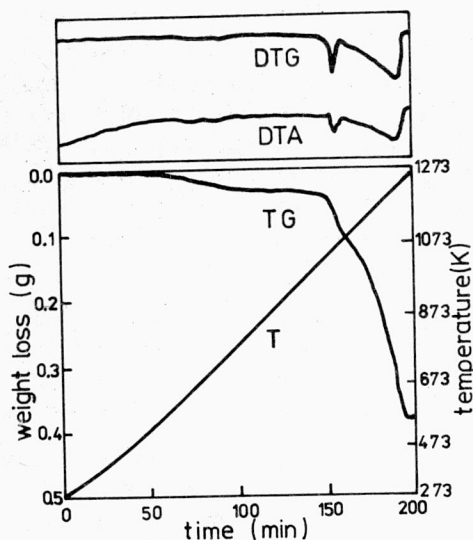


Fig. 1. Thermogram of raw dolomite (sample weight, 963 mg)

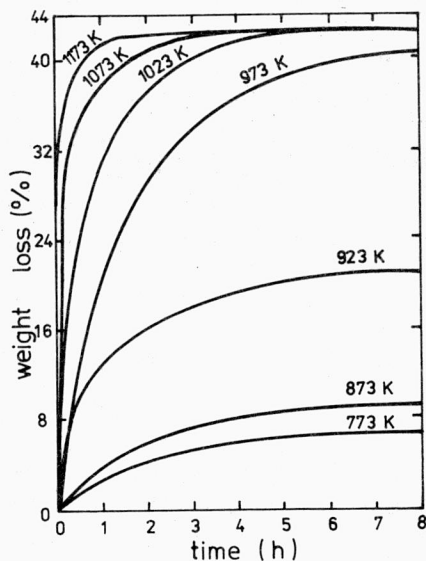


Fig. 2. Kinetics of thermal dissociation of dolomite

The total weight loss determined thermogravimetrically amounted to 40.5%. The DTG curve displays two minima indicating the temperatures at which the rate of conversion reached its maximal values. The two endothermic effects included in the DTA curve, at 1053 K and 1203 K, correspond with the temperature of dissociation for magnesium carbonate and with the temperature of complete dissociation for calcium carbonate, respectively. The highest weight loss obtained when studying the kinetics of thermal dissociation totalled 42.4% and was reached after 3 h at 1073 K. The difference in the dissociation temperature for dolomite results from the difference in the thermal conditions involved (linear increment of temperature, $5 \text{ deg} \cdot \text{min}^{-1}$, during thermogravimetric investigations, and constant temperature in the study of kinetics). The composition of the dolomite decarbonized via these routes is shown in tab. 1.

The objective of investigating the hydration process was to determine the reactivity of dolomite (after conversion into oxides) to the slaking water (i.e., the ratio of maximum temperature increment to the time of reaching it) and the degree of hydration (i.e., the ratio of dolomite weight increment to the stoichiometric amount of water required to hydrate calcium oxide and magnesium oxide). The reactivity of dolomite was related to the conditions of thermal dissociation and hydration. The plots are given in figs. 3 and 4. The highest reactivity ($4 \text{ deg} \cdot \text{s}^{-1}$) was that displayed

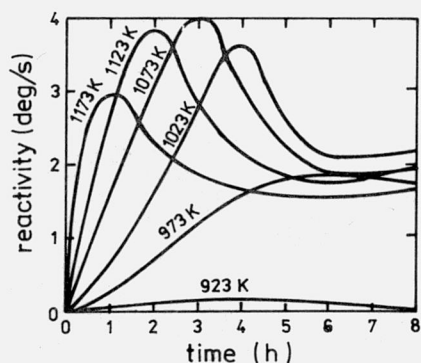


Fig. 3. Reactivity of dolomite at water: dolomite ratio of 2:1

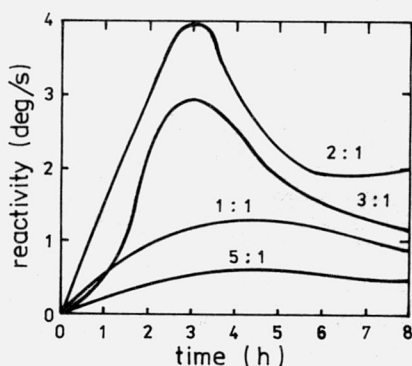


Fig. 4. Reactivity of dolomite dissociated at 1073 K as a function of water: dolomite ratio

by the mineral dissociated to oxides at 1073 K during 3 h and hydrated at a water: dolomite ratio of 2:1. Once a maximum had been reached, reactivity continued to decrease with the increasing temperature of dissociation. This holds for all the dolomite samples tested. The degree of hydration for the dolomite sample which exhibited the highest reactivity amounted to 98.6%. It was also the highest value achieved during the study. This indicates that both calcium oxide and magnesium oxide have been hydrated completely to hydroxides. A quick hydration of magnesium oxide should be attributed to the dolomite dissociation temperature, which

creates favourable conditions for a high activity of magnesium oxide. Another contributing factor is the utilization of heat produced during hydration of calcium oxide — provided that the amount of slaking water has been established adequately.

4.2. WATER TREATMENT

The efficiency of the dolomite coagulant was investigated by making use of model solutions with varied concentrations of coloured matter and turbidity. Optimum coagulant doses and optimum pH were determined for the purpose of colour and turbidity removal. More details can be found in the literature [9]. Experiments on model solutions have revealed that the treatment effects depend primarily on the influent turbidity level (samples of high turbidity, as well as compounds intensely coloured and of high turbidity) or on the degree of self-turbidity (samples intensely coloured). The efficiencies of colour and turbidity removal for three types of model solutions are plotted in figs. 5 and 6.

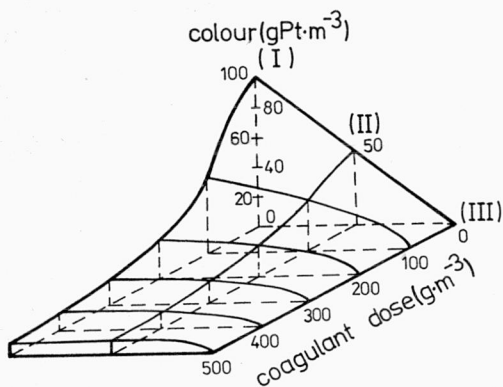


Fig. 5. Colour as a function of dolomite dose and initial colour intensity in model solutions

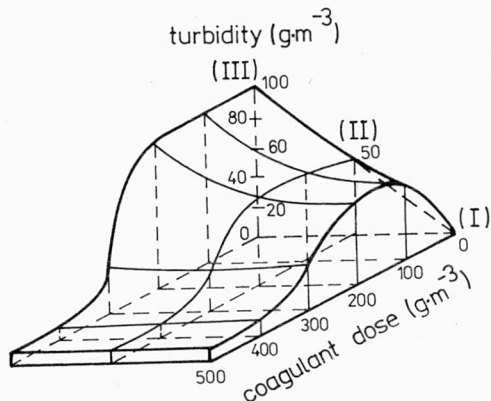


Fig. 6. Turbidity as a function of dolomite dose and initial turbidity of model solutions

Analysing the degree of coloured matter and turbidity removal from model solutions as a function of coagulant dose, it becomes obvious that the optimum dosage depends primarily on the efficiency of the clarifying process, which reaches a maximum at pH 10.5.

Experiments on model solutions have substantiated the high efficiency of dolomite when applied to remove colour and turbidity from an alkaline medium. However, of greater importance to engineering practice is the verification of the method on actual solutions, i.e., on natural surface-water samples. A typical physicochemical composition of natural water used for this purpose is given in tab. 2. In experiments on actual solutions the efficiency of the dolomite coagulant was investigated not only in relation to the removal of coloured matter and turbidity, but

Table 2

Chemical composition of the surface water (except pH, other values are in $\text{g}\cdot\text{m}^{-3}$)

Parameter	Average	Range
Turbidity	30	15-60
Colour as Pt	35	20-45
pH	7.2	6.9-7.4
Alkalinity as CaCO_3	120	60-150
Total hardness as CaCO_3	220	200-260
Chlorides as Cl^-	150	125-185
Sulphates as SO_4^{2-}	130	125-165
TOC	12.8	7.2-24.5
COD as O_2	10.2	5.6-21.5
TDS	700	520-920
Calcium as Ca	67.8	64.3-83.6
Magnesium as Mg	12.0	9.4-13.3

organics (in terms of TOC and COD as well. Turbidity and colour removal in water samples after sedimentation to a level of $10\text{ g}\cdot\text{m}^{-3}$ and $20\text{ g}\cdot\text{m}^{-3}$, respectively, was adopted as the criterion for the choice of the optimum coagulant dose. Besides dolomite, alum and lime were used as coagulants for the purpose of comparison. Figures 7 and 8 give average removal of TOC and COD achieved with these coagulants for surface-water samples. Thus, colour and turbidity removal was similar to that of model solutions. The optimum dolomite coagulant dose amounted to $300\text{ g}\cdot\text{m}^{-3}$, yielding complete colour removal and clear effluent. TOC and COD dropped by 65% and 60%, respectively. Analysis of data sets for various surface-water samples has shown that the optimum dolomite coagulant doses

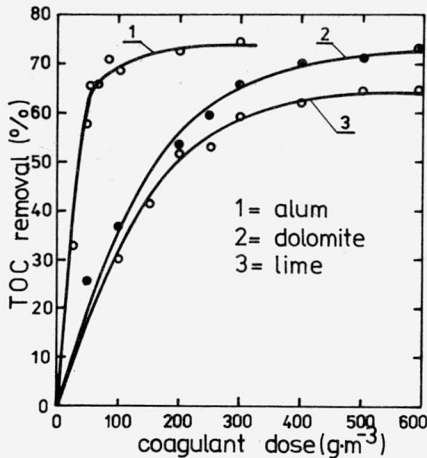


Fig. 7. TOC removal versus coagulant dose

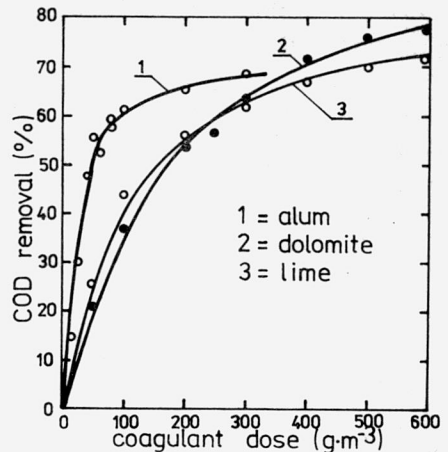


Fig. 8. COD removal versus coagulant dose

depend on the alkalinity level in the treated water (initial colour intensity and initial turbidity being negligible). Figure 9 relates the optimum coagulant dose to alkalinity. Again, the optimum dolomite dose is a function of influent alkalinity alone, but this happens only if initial coloured matter and initial turbidity are moderately high. The plots in fig. 10 describe the pH changes as a function of dolomite dose. As shown by

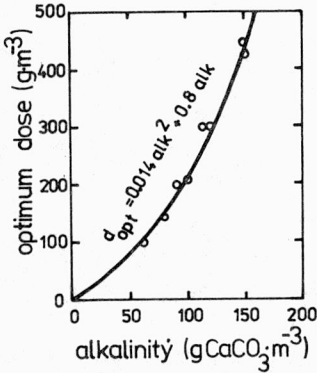


Fig. 9. Optimum dolomite dose versus alkalinity of raw water

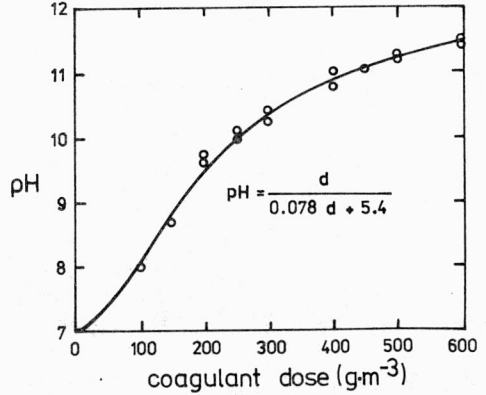


Fig. 10. pH versus dolomite dose

these data, the optimum pH for the treatment method in question is that of 10.5, which coincides with the results for model solutions. Apart from colour and turbidity removal, it is also the decrease of organic matter that contributes to the assessment of the dolomite coagulant efficiency. Analysing the reduction of TOC and COD in the presence of the dolomite coagulant, it becomes evident that the adsorption on calcium carbonate particles precipitated in water and on magnesium hydroxide particles incorporated in the coagulant is the main mechanism governing the removal of organics in this process. It is interesting to note that some part of organic matter persists in the effluent irrespective of the dolomite dosage applied. These non-removable fractions amount to 25% and 20% for TOC and COD, respectively, and are lower than those reported by REBHUN [5]. What seems to corroborate the adsorption mechanism governing the removal of TOC and COD in this technology is the possibility to describe the phenomenon adequately by using a generalized equation of isotherm derived for this purpose. Hence, we can write

$$X = \frac{K X_m (C_e - C_n)}{(C_0 - C_e) \left[1 + (K - 1) \frac{C_e - C_n}{C_0 - C_n} \right]}$$

where

X — adsorption capacity (number of grams of solute adsorbed per gram of dolomite at adsorbate concentration C_e),

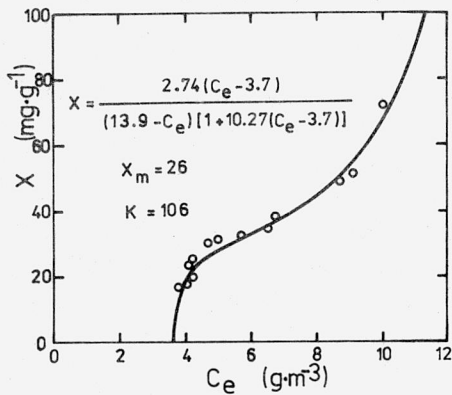


Fig. 11. Adsorption isotherm for TOC

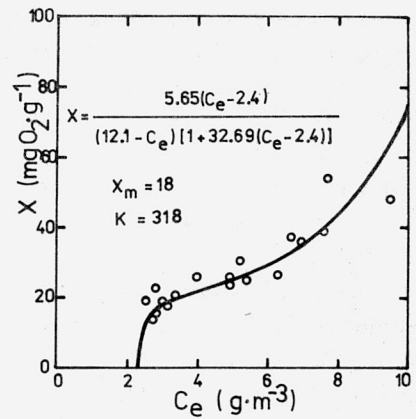


Fig. 12. Adsorption isotherm for COD

X_m – number of grams of solute adsorbed during the formation of a complete monolayer on the adsorbent surface,

K – constant expressing the energy of interaction with the surface,

C_0 – initial adsorbate concentration,

C_e – equilibrium adsorbate concentration,

C_n – non-removable adsorbate concentration.

The assumptions to the mathematical model, the derivation procedure and the verification of the formula derived via this route are given elsewhere [10]. Figures 11 and 12 show two isotherms of adsorption (along with relevant equations) for illustration.

The new technology of water treatment was also tested in a throughflow model system. Table 3 summarizes the test results (the determinations are means from

Table 3

Effluent quality at various treatment steps (except pH, other values are in $\text{g}\cdot\text{m}^{-3}$)

Water sample	Parameter					
	pH	Colour as Pt	Turbidity	Alkalinity as CaCO_3	COD as O_2	TOC
Raw water	7.2	35	40	120	12.1	13.2
After coagulation for $d = 300 \text{ g}\cdot\text{m}^{-3}$	10.5	10	5	135	4.3	5.2
After coagulation for $d = 200 \text{ g}\cdot\text{m}^{-3}$	9.9	20	30	90	7.3	8.6
After coagulation for $d = 250 \text{ g}\cdot\text{m}^{-3}$	10.2	10	5	95	4.7	5.4
After coagulation for $d = 250 \text{ g}\cdot\text{m}^{-3}$, recarbonation and rapid filtration	8.2	10	0	105	4.3	5.4

average hourly samples of a 12-hour cycle). The sludge-blanket clarifier included in the system enabled the optimum dolomite dose to be reduced from 300 to 250 g·m⁻³. Recarbonation (carried out after passage of the water through the clarifier in order to obtain the pH of stabilization) and rapid filtration had no effect on the concentrations of organics and coloured matter.

Filtration alone was found to be effective, yielding complete removal of suspended solids. The throughflow system approach also showed that the vertical velocity of water flow through the clarifier amounting to 2.5 mm·s⁻¹ was the highest achieved, when using a dolomite coagulant. The unit volume of precipitated sludge approached 2.5% in relation to the quantity of treated water. After 30 min of sedimentation, moisture content in the sludge amounted to 98.9%. Gravitational thickening during 2 h yielded a water content of 95.8%.

5. CONCLUSIONS

The experiments gave good support to the assumptions of the new technology for water treatment in an alkaline medium with dolomite as coagulant. The treatment method is a successful combination of softening, coagulation and adsorption. Since the last two processes have an important part in the system, the method may be defined as coagulation-adsorption.

Soft-burned and wet-slaked dolomite (wherein calcium hydroxide and magnesium hydroxide account for some 60% and 40%, respectively) is an effective coagulant, specifically when applied to systems of surface-water treatment involving sludge-blanket clarifiers. Sludge-blanket clarifiers yield better treatment effects with dolomite coagulants than alum because of the greater vertical velocity of water flow in the sludge layer produced by dolomite.

When concentration of influent coloured matter as well as turbidity are moderately high, the optimum dolomite dose depends on alkalinity alone. The optimum dosage varies from one natural water sample to another. In this study, it ranged between 100 and 400 g·m⁻³ to yield a clear and colourless effluent, as well as maximum values of TOC and COD removal. The optimum pH for the new technology approaches 10.5, and is much lower than that required for high-lime magnesium treatment. At pH 10.5, optimal treatment conditions are created, which not only enable good softening of water and good flocculation of calcium carbonate particles, but also prevent dissolution of magnesium hydroxide (entering the treated water together with the coagulant) and precipitation of magnesium (which is found in the influent water). The presense of magnesium in drinking water at concentrations of 30 to 155 g·m⁻³ is of prime importance to human health. Compared to lime treatment involving pH of about 11.5, the pH level of 10.5 required for the new

technology facilitates recarbonation, which may be a single-stage process under these conditions.

The principal mechanism governing the removal of organics (TOC and COD) in the technology of interest is adsorption on calcium carbonate precipitated in the water and on magnesium hydroxide included in the coagulant. Some part of the organic matter present in the water samples is resistant to removal by this method. However, the values of non-removable TOC and COD are distinctly lower than these in the lime-coagulation process. The equation of multi-layer isotherm, which includes the non-removable adsorbate concentrations, lends itself well to the modelling of organic matter removal by the new technology.

The dolomite coagulation-adsorption technology may be recommended for the treatment of practically all types of surface waters that are to be used either for industrial needs or municipal supply. The management of precipitated sludge produced by this method has been well described in the available literature and raises no technical problems.

Basic research on the structure of calcium carbonate and magnesium hydroxide particles and their contribution to the coagulation-adsorption of various pollutants present in both water and wastewater is underway. The results will hopefully permit a joint estimation of the new technology, thus extending its range of application to the chemical treatment of wastewater or to water reuse.

ACKNOWLEDGEMENT

This paper was developed from a study supported by Governmental Project No. PR-7.

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Translated by Janina Kosińska

TECHNOLOGIA OCZYSZCZANIA WODY METODĄ KOAGULACJI-ADSORPCJI DOLOMITEM

Przedstawiono zasady i parametry nowej technologii oczyszczania wody, w której jako koagulant zastosowano odpowiednio przetworzony dolomit zawierający głównie wapń i magnez w postaci wodorotlenków. Technologię tę opracowano na podstawie badań laboratoryjnych, które pozwoliły określić podatność roztworów modelowych oraz wód naturalnych na oczyszczanie koagulantem dolomitowym. Parametry otrzymywania koagulantu z surowego dolomitu określono badając jego termiczny rozkład i hydratację. Efektywność technologii oczyszczania wody oceniono na podstawie przebiegu odbarwiania i klarowania wody oraz usuwania z niej związków organicznych (OWO, utlenialność).

Opracowana technologia jest bardzo skuteczna w oczyszczaniu wód powierzchniowych o różnym stopniu zanieczyszczenia. Oprócz pełnego odbarwienia i sklarowania wody uzyskuje się także duży stopień usunięcia związków organicznych, metali ciężkich oraz mikrozanieczyszczeń, a także częściową dezaktywację wirusów i bakterii. Optymalna dawka koagulantu dolomitowego zależy głównie od zasadowości wody, gdy jej mętność i barwa są umiarkowane, a optimum pH procesu oczyszczania wynosi 10,5. Woda oczyszczona tą metodą jest, po rekarbonizacji jednostkowej, całkowicie stabilna i niekorozyjna.

Nowa technologia oczyszczania wody łączy w sobie w sposób korzystny trzy procesy jednostkowe: dekarbonizację, koagulację i adsorpcję.

ТЕХНОЛОГИЯ ВОДООЧИСТКИ МЕТОДОМ КОАГУЛЯЦИИ-АДСОРБЦИИ ДОЛОМИТОМ

Представлены принципы и параметры новой технологии водоочистки, в которой в виде коагулята применили обработанный доломит, содержащий, главным образом, кальций и магний в виде гидроокисей. Технология очистки разработана на основе лабораторных исследований, которые позволили определить податливость модельных растворов и природных вод на очистку доломитовым коагулянтом. Параметры получения коагулянта из сырого доломита определено исследуя его термическое распределение и гидратацию. Эффективность технологии водоочистки оценено на основе хода отбеливания и осветления воды и удаления из неё органических соединений (OWO, окисляемость).

Разработанная технология является очень эффективной в очистке поверхностных вод с разной степенью загрязнения. Кроме полного отбеливания и осветления воды, получен также высокий уровень удаления органических соединений, тяжёлых металлов и микрозагрязнений, а также частичная дезактивация вирусов и бактерий. Оптимальная доза доломитового коагулянта зависит от оснóвности воды, когда её мутность и цвет умеренны, а оптимум [рН] процесса очистки равняется 10,5. Очищенная этим методом вода, после одноступенчатой рекарбонизации, является полностью устойчивой и некоррозийной.

Новая технология водоочистки совмещает в себе полезным способом три единичных процесса: декарбонизацию, коагуляцию и адсорбцию.