Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

ISSN: 0972-6268	Vol. 14	No. 4	pp. 947-950	2015

Original Research Paper

Wastewater Treatment of Industrial Enterprises Using Carbonate Sludge

A. Nikolaeva Larisa, G. Laptev Anatoliy and Ya. Iskhakova Regina†
Kazan State Power Engineering University, 51, Krasnoselskaya str., Kazan, The Republic of Tatarstan, Russia, 420066
†Corresponding author: Ya. Iskhakova Regina

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com
Received: 07-04-2015
Accepted: 05-05-2015

Key Words:
Wastewater treatment
Carbonate sludge
Low cost adsorbent
Biological sorption

ABSTRACT

In the present article, a perspective method of biological sorption process of wastewater treatment in the chemical industry is reviewed. This article focuses on the carbonate sludge produced by heat power stations that is used as a sorption material, and adsorption properties of carbonate sludge and its influence on activated sludge are considered. Sludge is a micro and mesoporous sorbent, which is confirmed by the sorption curves for formaldehyde and ammonia nitrogen. Removal of ammonia nitrogen and reduction of COD and BOD_5 in aqueous solutions by means of carbonate sludge was investigated. It was observed that the maximum removal of COD, BOD_5 and ammonium nitrogen was achieved at 600 mg/L dosage adsorbent carbonate sludge. This dose helped to reduce COD in water by 91% on the average, BOD_5 by 98% and ammonium nitrogen by 94%. It was found that the biological sorption process is more effective than biological wastewater treatment. A modified biological wastewater treatment line was submitted to the Kazan Synthetic Rubber Plant (Russia).

INTRODUCTION

Nowadays, a problem of reducing anthropogenic impact on the environment has become very important. Wastewater treatment is crucial, because every industry involves water in various processes. Biological wastewater treatment is a conventional stage based on natural vital processes of microorganisms.

Contemporary approaches to wastewater treatment, allow modifying the biological treatment stage by combining it with other methods to increase the efficiency and profitability of the process. One of such methods is the adsorption method providing wastewater treatment and reduction of impurities. Carbonate sludge formed during natural water pretreatment on a heat-power station (HPS) can be considered as a cheap and effective sorbent.

MATERIALS AND METHODS

The materials of the experiment were carbonate sludge-waste of HPS, industrial wastewater of Synthetic Rubber Plant in Kazan (Russia), distilled water, formalin, ammonium nitrate, etc.

Wastewater analysis was carried out at Kazan Synthetic Rubber Plant (KSRP) and Kazan State Power Engineering University (Russia).

Carbonate sludge is a natural water lime-treatment and coagulation product. Dried sludge is a powdery finely dispersed material coloured from light yellow to brown. The chemical composition of the sludge is mainly calcium carbonate (Table 1) (Nikolaeva et al. 2012). The method of gas chromatography-mass spectrometry showed that the contents of humic acid in the carbonate sludge are up to 12%.

The results of the grain size sieving-based analysis showed that the average size of a fraction is 0.09-1.5 mm. The bulk density of this fraction is 0.61 g/cm^3 (according to GOST 2093-82, 2001).

Previously, the specific surface of the sludge was found as 22 m^2/g (Boroday 2011). Carbonate sludge is a waste, and it can be used as a sorption material for wastewater treatment, which makes it extremely perspective.

Carbonate sludge was evaluated for its formaldehyde and ammonia nitrogen removal capacity from an aquatic medium. Sorption capacity of formaldehyde on sludge was determined using the sulphite method (GOST 1625-89, 1997); the sorption capacity of ammonia nitrogen was determined using the titrimetry method using the preliminary distillation of ammonia to boric acid solution (GOST 29304-92, 2004).

The purpose of this research is to increase the quality of the industrial wastewater treatment via the biological sorption technology. For that purpose, a laboratory setup was used. Real wastewater of Kazan Synthetic Rubber Plant (KSRP) was treated. The diagram illustrating the laboratory setup is shown in Fig. 1. In parallel, the researches on biological wastewater treatment by means of activated sludge in the control setup were conducted (Nikolaeva et al. 2010).

Wastewater was fed to the sample aeration tank 1 hav-

Table 1: Chemical composition of sludge.

Mineral part The concentration of compounds, % (wt.) Cations		Anions	
Ca^{2+}	76.56± 11.3	CO_3^{2-}	71.7±10.6
Fe^{3+}	0.38± 0.15		
Mg^{2+}	9.7± 2.2	SO_4^{2-}	5.7±0.85
Cu^{2+}	0.04± 0.014		
Ni^{2+}	0.008± 0.003	OH^-	10.03±3.61
Zn^{2+}	0.033±0.013		
Mn^{2+}	1.05± 0.407	SiO_3^{2-}	0.52±0.11
Cr^{3+}	0.001± 0.0003		
Pb^{2+}	0.002± 0.0003	PO_4^{3-}	-
Cd^{2+}	0.22± 0.08		

Organic part- 12 % (wt.)

ing the concentration of dissolved oxygen of 4.2 mg/dm^3. The total volume of the setup was 10 dm^3. Dried carbonate sludge with constant humidity of 3% was dosed to the aeration tank. Activated sludge concentration was 1.5-2.0 g/dm^3. Wastewater with suspended particles stayed in the aeration tank for 12 hours and then was flown by gravity into the secondary settling tank 2 to separate the sludge mixture from wastewater in 2 hours.

COD was determined by (GOST R 52708, 2007) and BOD_5 by (PND F 14.1: 2.3.4.123-97, 2004).

The initial wastewater quality indicators were: COD-330 mg O_2/dm^3, BOD_5-95 mg O_2/dm^3, ammonia nitrogen-1.6 mg/dm^3. During the simulation, dried sludge was dosed to an aeration tank in the amount of 100 to 900 mg/dm^3. The research used sieved sludge with fractions of 0.09-0.50 mm.

The environmental and toxicological assessments of the biological sorption wastewater treatment using carbonate sludge (600 mg/dm^3) were conducted. Express-testing was conducted to determine acute lethal toxicity of substances to the fishes (species *Poecillia reticulata* Pet.) and the crustaceans (*Daphnia magna* Str.) (Miheev 2001).

The experiments based on establishing the differences between the number of dead organisms in the test sample and in the control sample were performed (GOST R 52708, 2007).

RESULTS AND DISCUSSION

The sorption isotherms of the investigated contaminants: Formaldehyde adsorption isotherm on carbonate sludge belongs to the V type according to the BET classification (Fig. 2). This type of S-shaped isotherms show the availability of micro and mesopores in the sorbent. The initial concavity indicates a weak intermolecular interaction between the sorbent and the sorbate. A further change in the

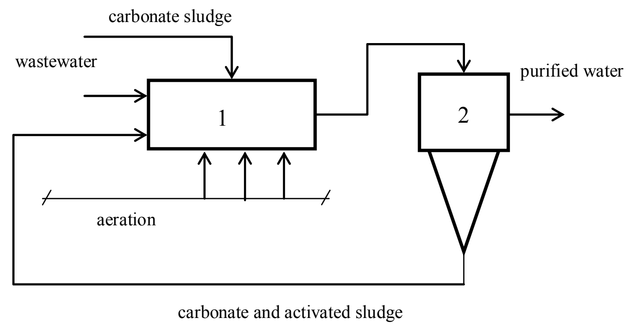

Fig. 1: Laboratory setup of treatment plant.

curve is caused by capillary condensation in the adsorbent pores and the formation of a polymolecular layer on the sludge surface.

The resulting isotherm is presented in logarithmic scale in Fig. 3.

The isotherm is described by Freundlich's equation:

$$\lg x/m = 0.74+0.509\lg Ce$$

$$x/m = 5.5Ce^{0.51}$$

The ammonia nitrogen sorption isotherm is shown in Fig. 4. The adsorption isotherm is of type I according to the BET classification. Therefore, the carbonate sludge contains micropores. The initial portion of the curve is described by linear dependency of the Henry's law. The curve then goes to the equilibrium, which conforms to the Langmuir's theory of the monolayer formation on the sorbent surface. As ammonia nitrogen concentration increases, the sludge saturates and reaches the sorption equilibrium. The adsorption capacity of the material for ammonia nitrogen is 2.6 mg/dm^3.

The sorption isotherm of ammonia nitrogen in logarithmic form is shown in Fig. 5.

The isotherm is described by Freundlich's equation**.**

$$\lg x/m = 0.414 + 0.521\lg Ce$$

$$x/m = 2.59Ce^{0.52}$$

Therefore, the curves display the possibility of using sludge as a sorption material to improve the quality of biological wastewater treatment.

During the research, the dependency of COD, BOD_5 and ammonia nitrogen on the added sludge's concentration was examined. Quantitative measurements of pollutants were carried out by using samples from the secondary clarifier tank. It was experimentally established that the optimal dose of injected sludge is 600 mg/dm^3. This dose helps reducing COD in water by 91% on the average, BOD_5 by 98 % and ammonium nitrogen by 94%. After conducting biological sorption treatment, the quality of wastewater treatment result meets the quality criteria of Kazan Synthetic Rubber Plant.

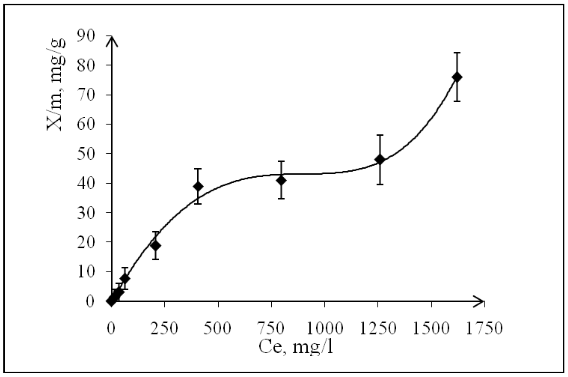

Fig. 2: Formaldehyde sorption isotherm.

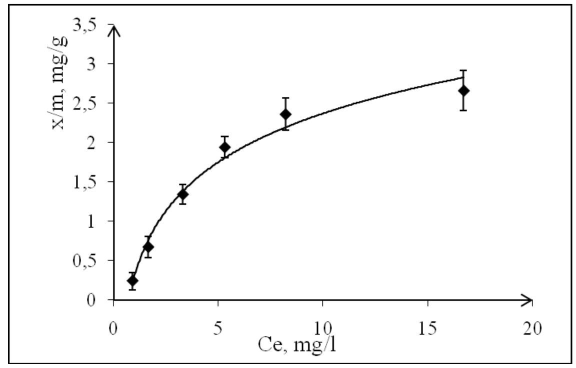

Fig. 4: Ammonia nitrogen sorption isotherm.

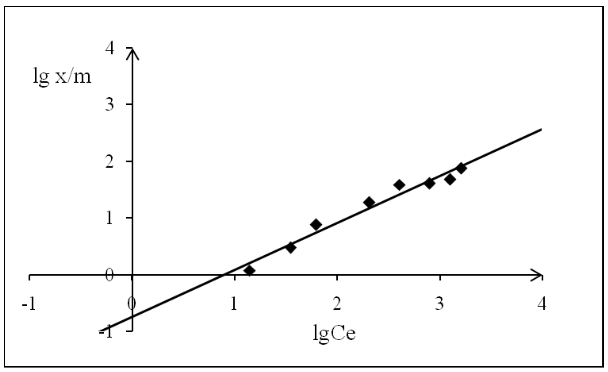

Fig. 3: Logarithmic form of the formaldehyde sorption isotherm.

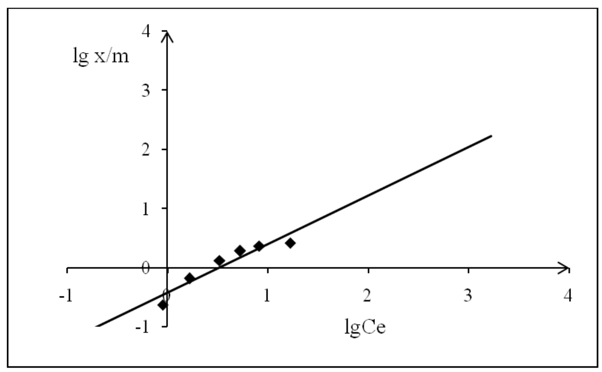

Fig. 5: Logarithmic form of the ammonia nitrogen sorption isotherm.

The kinetic dependency of the COD, BOD_5 and ammonia nitrogen concentrations are shown. It was determined that the wastewater treatment process goes intensively in the first hours after contact with wastewater, and after 4 hours the contaminant concentration only changes slightly. Abrupt decrease of the organic wastewater contaminant concentration in the early hours indicates the physical sorption. Further gradual decline is caused by biological oxidation.

The COD's kinetic curve indicates that within the first 2 hours after contacting with wastewater, the biological sorption process has maximum intensity. An abrupt decrease of COD is caused by sorption of organically non-degradable components by sludge. During the first 4 hours, intensive decline of BOD_5 becomes more gradual. It happens because of the attached biofilm increasing the efficiency of cleaning from organic contaminants.

Efficient removal of ammonium nitrogen is caused by more complete and rapid removal of organic contaminants and by the presence of solid porous mineral material. The pH value shifted towards alkalescent medium also promotes intensive growth and activity of nitrifying bacteria.

The results of the toxicological analysis revealed that the dosing of sludge has no acute toxic effects. The percentage of surviving fishes was 100% and the percentage of dead daphnia-below 50%.

The results of the experimental research envisage the modified technology of KSRP's wastewater treatment (Fig. 6; 1-sand trap, 2-screens, 3-liquidizer, 4-primary settling tank, 5-aeration tank, 6-secondary settling tank, 7-storage of carbonate and activated sludge after the secondary settling tank, 8-storage of sludge after the primary settling tank, 9-disinfecting unit, 10-chamber, 11-sand bunker, 12-wet carbonate sludge bunker, 13-belt drier, 14-disintegrator, 15-store bunker, 16-automatic spreader).

The upgrade of the existing technology of wastewater treatment requires installing a wet carbonate sludge bunker (60% moisture) (12), a belt dryer (13) and a disintegrator (14), a store bunker (15), an automatic spreader batcher (16).

The sludge is delivered to the bunker (12) by motor transport. The bunker is connected to the screw feeder. The bunker is equipped with a channel to remove moisture from the melted ice, which is contained in the sludge (in winter). The screw feeder dispenses sludge to the belt dryer (13).

The belt dryer (13) is a multilevel perforated conveyor belt, on which the dried product is felt out from the upper

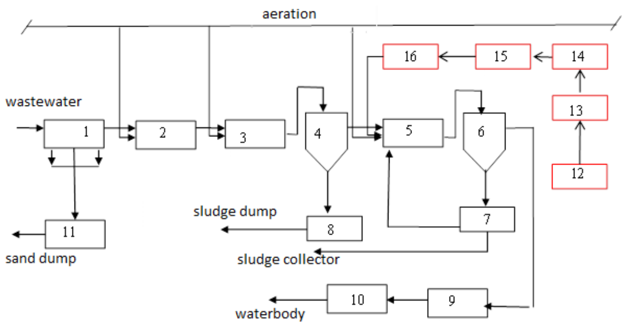

Fig. 6: The modified technology of KZRP's wastewater treatment.

level to the subsequent level. The conveyor belt moves at a speed of 0.3-0.5 m/min. Sludge falls down from upper to lower levels and overturns, which results in improved drying efficiency.

The air from the fan heater works as a drying agent. The heated air passes through the perforated conveyor belt and a layer of sludge. Air velocity does not exceed 1.5 m/s. The sludge is dried at the temperature of 120°C.

The dried sludge is fed to the disintegrator (14). The disintegrator is used to shred sludge particles down to a size not exceeding 0.1 mm (suitable for milling of limestone). The dried milled sludge is fed by the screw feeder to the store bunker (15) designed to hold different volumes of output.

The prepared sludge is fed to the automatic spreader device (16) by lift trucks. The spreader is a two-disc centrifugal machine powered by the electric drive designed to inject carbonate sludge to the aeration tank (5) surface. The principle of operation of the spreader is as follows: Sludge from the bunker (15) is fed to a centrifugal disc which dispatches it as a fan-shaped flow over the surface of the water across the width of the aeration tank. Discs are made of stainless steel with adjustable speed (up to 706 rev/min) and with a possibility to change the tilt angle of the disk.

In the aeration tank (5), biological sorption wastewater treatment is performed. Further, carbonate and activated sludge are fed to the secondary clarifier (6). Part of it is sent to the regenerator (5). Remaining activated and carbonate sludge is dispatched to the sludge collector.

Using sludge as a secondary material resource, provides its utilization and solves the problem of reducing the anthropogenic effect. New approaches to carbonate sludge utilization can be used to improve the hydrochemical condition of the nearby water objects, to reduce mineralization of groundwater and to solve the problem of soil salinization. Also, they allow to reduce running costs of HPS related to the waste accumulation and storage. Using carbonate sludge as a sorption material, on biological wastewater treatment stage in the aerotank, is proposed.

Therefore, carbonate sludge can be used as a sorption material for biological sorption treatment of industrial wastewater together with activated sludge microorganisms. Using HPS wastes helps achieving several goals:

1. Intensifying the biological wastewater treatment process, improving the quality of water without changing the design of existing devices (aeration tank and secondary clarifier).
2. Reducing running costs of biological wastewater treatment of KSRP.
3. Conducting an effective waste management on a heat-power station.

ACKNOWLEDGEMENTS

The study was carried out in the context of the Governmental task in the scientific area. Application No. 13.405.2014/K "Energy and resource conservation and reducing of anthropogenic effect on environment in the fuel-power complex".

REFERENCES

Boroday, E. N., 2011. Resource-saving technology of water treatment sludge disposal at heat-power station. Thesis for the degree of Ph.D., pp. 115. (in Russian).

GOST 29304-92, 2004. Ammonium nitrate technical. A method for determination of ammonia nitrogen (titrimetric) after distillation. Moscow: Publishing Standards IEC., pp. 6 (in Russian).

GOST 1625-89, 1997. Formalin technical. Specifications, pp. 17 (in Russian).

GOST 2093-82, 2001. Solid fuel. Sieve method for determining the granule metrical composition. Moscow: Publishing IEC standards, pp. 20 (in Russian).

GOST R 52708, 2007. Water. Method for determination of chemical oxygen demand, Moscow: Publishing IEC standards, pp.11 (in Russian).

Miheev, N.N. (ed.) 2001. Guidelines for the determination of waters, sediments, pollutants and drilling fluids toxicity. Moscow: REFIA. pp. 102 (in Russian).

Nikolaeva, L.A. and Iskhakova, R. Ya. 2012. Sewage treatment of industrial enterprises on the basis of biosorption technology. Thermal Engineering, 3: 78-80 (in English).

Nikolaeva, L.A., Sotnikov, A.V. and Iskhakova R. Ya. 2010. Sorption-properties of carbonate sludge in biological wastewater treatment of industrial enterprises. Energy of Tatarstan. 3: 76-80 (in Russian).

PND F 14.1: 2.3.4.123-97, 2004. Quantitative chemical analysis of water. Methods for determination of biochemical oxygen demand after the 5-days incubation, pp. 14 (in Russian).