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COAGULATION OF COAL GASIFICATION WASTEWATERS

1. INTRODUCTION

Coal gasification produces wastewater that contains ammonia, dissolved organics, cyanides and other contaminants which have a high pollution potential if released to the environment or are highly corrosive and fouling if not treated before reuse [1]. In the coking industry, which produces an effluent similar to coal conversion wastewaters, biological treatment has been used successfully for many years in conjunction with other physical–chemical treatment processes.

Pretreatment methods, including dilution, were found by SINGER et al. [2] to be necessary in treating synthetic coal conversion wastewater. A large portion of impurities present in coal gasification wastewater are in the colloidal form which cannot be removed by gravity settling. Chemical coagulants can be added to form larger, more readily settleable aggregates in which these impurities are enmeshed as described by GOOS et al. [3]. The type of primary treatment employing a coagulation–sedimentation process is often used to reduce the concentration of impurities to an allowable level before the wastewater is treated biologically. The most extensively used coagulants for wastewater treatment are aluminum and iron salts. The objectives of this study were to determine the types and dosages of coagulants and optimum pH required for effective coagulation.

2. MATERIALS AND METHODS

The slagging fixed-bed gasifier at the U.S. Department of Energy Grand Forks Energy Technology Center (GFETC) is the only unit of its type in the U.S.A Coal is fed through a lock hopper and gravity fed into the gasifier. As the coal enters the gasifier, it is heated, dried and carbonized by hot rising gases. Carbonized coal (char) is contacted with an oxygen–steam mixture just above the hearth and combustion occurs. A hearth temperature of about 3100° F is high enough to consume the coal completely and convert the ash to slag. The slag drains through a tap hole and is cooled in a water bath. Raw product gas steam is contaminated with tars, light oils, water, and other volatile materials. The light oil, water, tar, and dust are removed by scrubbing with a spray of recycled gas liquor. A second scrubber is used to further refine the product gas. All wastewater is directed to a receiver where a gravity separation of low boiling

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tars occurs. The wastewater used in this study was obtained from the gasification of lignite from the Indianhead mine (Mercer County), North Dakota, U.S.A.

Samples used in this investigation were collected from the gas liquor receiver at GFETC and stored in 5 gallon plastic containers at 0° C. The pretreatment sequence included lime precipitation, air stripping, and coagulation. Wastewater was prepared for ammonia stripping by addition of lime which reduced alkalinity and increased pH to 12. Lime and gas liquor were mixed for 10 minutes then allowed to settle for several hours. The supernatant was air stripped until ammonia nitrogen concentration was reduced to less than 500 mg/dm^3.

Gasifier wastewater contains suspended and colloidal materials. Coagulants used to reduce these contaminants included aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$), ferric chloride ($FeCl_3 \cdot 6H_2O$), ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), lime ($CaO$), and activated carbon (HD-4000). A six--place laboratory stirrer manufactured by Phipps and Bird, Inc. was used in the jar-test for coagulation study.

Coagulants were added to the wastewater followed by rapid mixing for three minutes at a paddle speed of 100 rpm, and then by slow mixing for 30 minutes at 20 rpm. The flocculant material was allowed to settle for at least 30 miniutes before a sample of the supernatant was withdrawn for laboratory analyses. Dosages of coagulant up to 25 g/dm^3 were added to the wastewater. Parameters selected for measurements of the effects of coagulation include transmittance, pH, phenol, and biochemical oxygen demand (BOD). The transmittance was used as an indication of clarity of treated effluents and effectiveness of coagulation. A Bausch and Lomb Spectronic 20 was used for the measurement of transmittance at wavelength of 550 nm. BOD and phenol were determined using procedures described in the standard methods by the American Public Health Association [4].

3. RESULTS AND DISCUSSION

Samples of coal gasification wastewater were firstly treated using lime (CaO) as a coagulant. It was noted that the supernatants were rarely cleared up for the determination of percent transmittance. However, the lime coagulation did show its noticeable effect on phenol concentration in the wastewater. With the initial concentration of phenol of 4000 mg/dm^3, the phenol removal of 28% was obtained at a lime dosage of 20 g/dm^3. The phenol concentration was reduced to 2900 mg/dm^3.

The variation of biochemical oxygen demand (BOD) values of coal gasification wastewaters with time and sample sizes is shown in fig. 1. It was found that the BOD generally increased rapidly with time for the first five days, then increased slowly for the next five days, and stayed nearly the same afterward. The BOD curve for the small sample size of 50 μl showed a different trend of BOD exertion. It had a continuously rapid increase of BOD for ten days then leveled off, and BOD remained very high afterward. As time exceeded over ten days, the small sample size had the highest BOD and the large sample size (200 μl) had the lowest BOD. The higher the dilution of coal gasification wastewaters, the higher the BOD values. This indicated that the coal gasification wastewaters contained toxic substances which inhibited bio-oxidation as shown in the BOD exertion. The BOD shown in fig. 1 was the total one and consisted of both carbonaceous BOD and nitrogeneous BOD.

In order to determine the carbonaceous BOD present in coal gasification wastewaters, methylene blue was added to the wastewaters to inhibit nitrification by nitrifiers. Figure 2 depicts the carbonaceous BOD exertion versus time. A similar trend as mentioned in fig. 1 was noticed.The difference between the total BOD and the carbonaceous BOD is the nitrogeneous BOD, which is the BOD exerted by the nitrifiers during the nitrification process. From comparison of figs. 1 and 2, it can be seen that significant nitrification occurred in the smallest sample sizes of 50 μl. For larger sample size of 100, 150, and 200 μl, the nitrification appeared to be inhibited. Since coal gasification wastewaters contained high concentration of ammonia and phenol, it is possible that these compounds may inhibit nitrification.

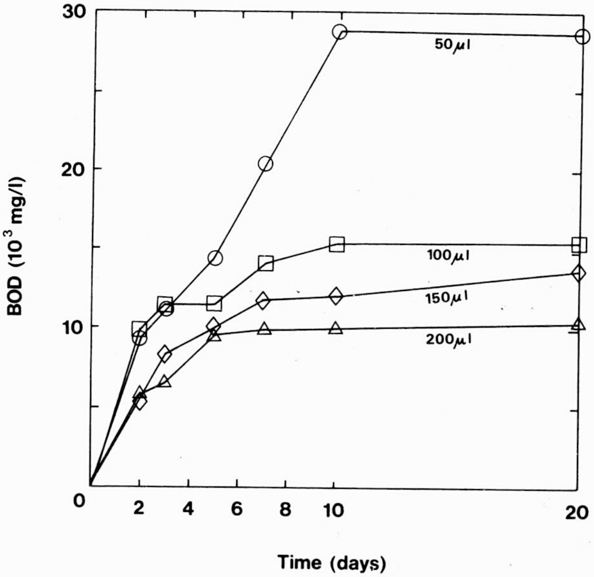

Fig. 1. BOD vs. time without addition of methylene blue

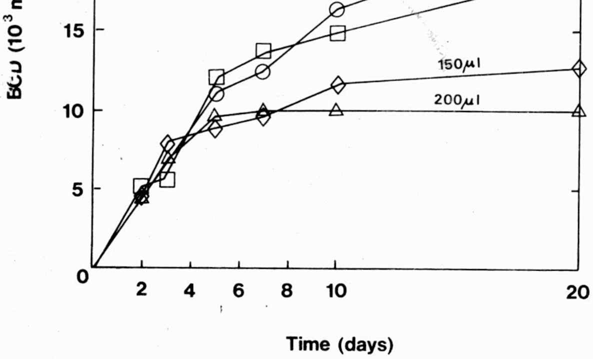

Fig. 2. BOD vs. time with addition of methylene blue

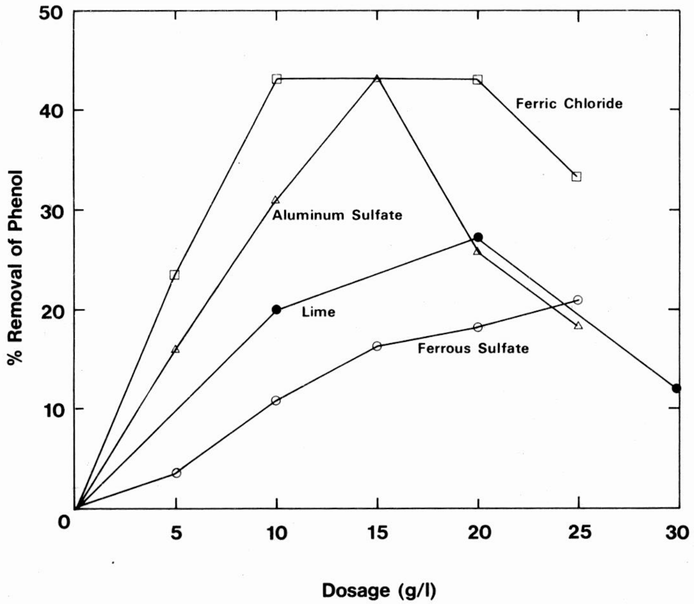

Fig. 3. % Removal of phenol vs. coagulant dosage in treating lime precipitated and ammonia stripped wastewater

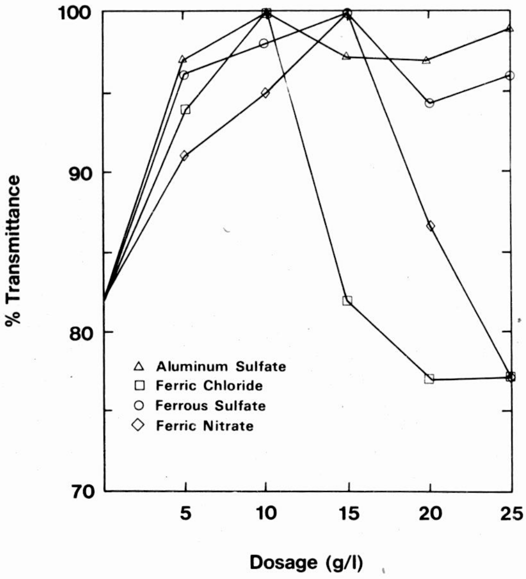

Fig. 4. % Transmittance vs. coagulant dosage in treating lime precipitated and ammonia stripped wastewater

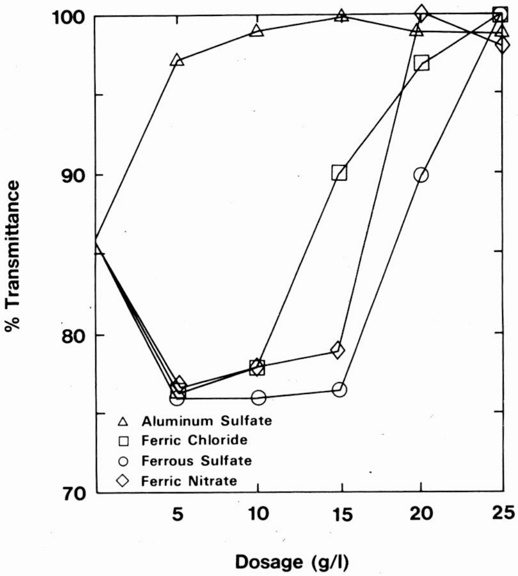

Fig. 5. % Transmittance vs. coagulant dosage in treating lime precipitated wastewater

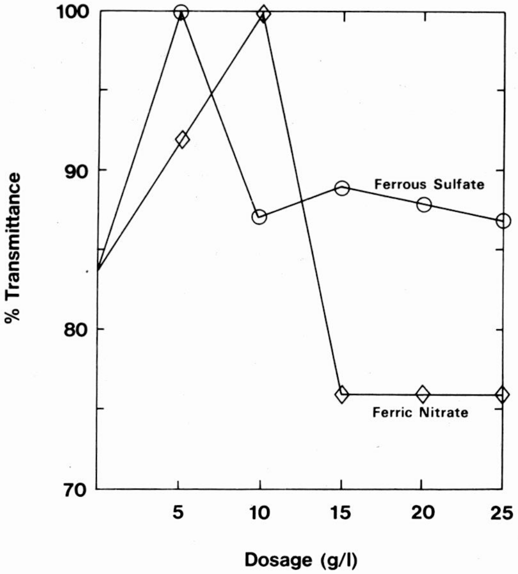

Fig. 6. Effect of aging on the coagulation of lime precipitated and ammonia stripped wastewater

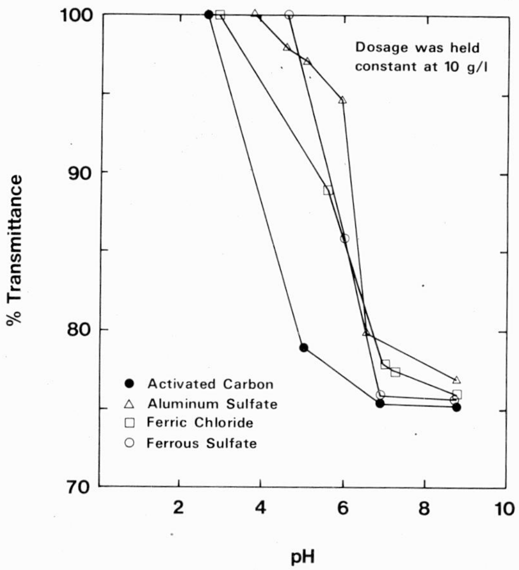

Fig. 7. Effect of pH on the coagulation of lime precipitated and ammonia stripped wastewater at a constant dosage

The result of coagulation of the lime precipitated and ammonia stripped wastewater for phenol removal is shown in fig. 3. It was found that the ferric chloride was the best coagulant, at a dosage of 10 g/dm^3 it removed 43.2% of the initial phenol concentration. Aluminum sulfate had a maximum removal of 43.2% at a dosage of 15 g/dm^3, and lime had the highest removal of 27.5% at 20 g/dm^3 dosage. Ferrous sulfate was least effective, removing only 20% of initial phenol content. Percentages of transmittance versus dosages for various chemical coagulants are plotted in fig. 4. On the basis of percent transmittance, aluminum sulfate and ferric chloride had an optimum dosage of 10 g/dm^3 for their highest amount of clarity. The optimum coagulant dosage for ferrous sulfate and ferric nitrate was 15 g/dm^3. It was also found that the ferric chloride and ferric nitrate presented a higher clarity of the supernatants. The aluminum sulfate samples possessed a yellowish supernatant, while the ferrous sulfate samples showed a low degree of clarity. Figure 5 shows the variation of transmittance with dosage for various coagulants in treating the lime precipitated wastewater. Aluminum sulfate provided a very clear supernatant for all dosages greater than 5 g/dm^3. Ferric chloride and ferric nitrate did clear to some degree at higher dosages, but did not possess as much clarity as the aluminum sulfate sample. Once again the ferrous sulfate did not clear at all.

The effect of the aging of the coagulation of lime precipitated and ammonia stripped wastewater was tested using the ferrous sulfate and ferric nitrate. Samples of wastewater were 20 days old prior to the treatment. As shown in fig. 6, the ferrous sulfate had a highest degree of clarity at an optimum dosage of 5 g/dm^3, while the ferric nitrate had its optimum dosage at 10 g/dm^3. The variation pattern of transmittance for both the ferrous sulfate and ferric nitrate seemed to be similar for the old wastewater as the new, but the optimum dosage of these chemical coagulants in the aged wastewater was decreased by 5 g/dm^3. A set of jar tests were carried out to examine the effect of pH on the coagulation of the lime precipitated and ammonia stripped wastewater. Coagulants used included aluminum sulfate, ferric chloride, ferrous sulfate, and activated carbon (HD-4000). Dosage was held constant at 10 g/dm^3. The result of percent transmittance versus pH is shown in fig. 7. The optimum pH of coagulation for aluminum sulfate was at low pH of 3.0–5.0. The iron compounds were effective at any pH below 6.0 and the activated carbon was good at pH of 3.0. The optimum pH was 4.0 for aluminum sulfate. The activated carbon did not produce a heavy floc for any value of pH, which was probably due to the low dosage of application in the investigation.

4. CONCLUSIONS

In removing the phenol from the coal gasification wastewaters, ferric chloride proved to be the best coagulant, and lime was not a good coagulant. It is also found that ferric chloride and ferric nitrate were very effective in increasing the transmittance of the coal gasification wastewaters, while ferrous sulfate was ineffective in improving the clarity of the wastewaters.

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