Carwash wastewater purification before its discharge into municipal sewer

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Abstract. The paper demonstrates that car service stations and their wastewater heavily pollute the environment. The research shows that this wastewater can be cost-effectively purified up to the standards applied to circulating water supply of similar enterprises. Keywords: circulating water supply, maximum allowable concentration (MAC), reagent sedimentation, electroflocculation, purification technology. The analysis of the obtained results shows that the water clarification effect was very high. Comparing two kinds of filtering loads shows that vermiculite is more preferable and effective because its purification effect is more apparent than that of brucite. Besides, vermiculite partially removes the smell of the wastewater drainage. In addition, the use of AA allows one to significantly reduce the salt load on reservoirs and watercourses and keep the pH value within the required MAC.

1. Introduction

Modern car service stations (CSS) usually include car wash facilities, assembly site, paint-and-varnish department (PVD) and anti-corrosion car-body treatment workshop. These facilities are often located in residential areas. Technological and surface run-off formed at CSS are often discharged into nearby storm water drainage system as "clean-contaminated" without any purification [1-14].

The composition of these effluents and their discharge result either in water bodies eu-trophication or in additional unjustified loads for sewage treatment plants located in residential areas.

2. Problem Specification

Papers [15,16] describe several methods of determining fat concentration in wastewater. The describes are based on the extraction of fats and oils by means of organic solvents.

The researchers examined wastewater of each workshop of JSC "Samara-Lada". Physico-chemical analyses were carried out in a certified hydrochemical laboratory of the Water Supply and Wastewater Disposal Department, Samara State Technical University. 20 to 24 water samples were selected from discharge channels of each workshop.

Table 1 sums up the results of these samples analysis. It is shown that:

1. The water consumed for production needs is characterized by its irregular distribution to sewage treatment plants and by considerable fluctuation of pollution concentration (for example, suspended substances difference reaches 200 times). The main contaminants in CSS production wastewater are suspended substances, oil products, surfactants, iron and heavy metals (copper, zinc, cadmium, lead).
Table 1. Composition of CSS wastewater drainage.

| Parameter                                      | MAC   | Car wash | Workshop values | Assembly site |
|-----------------------------------------------|-------|----------|-----------------|---------------|
|                                               |       | Average  | E, times | D, %         | Average  | E, times | D, %         |
| Hydrogen parameter, pH                        | 6.5-8.5 | 7.30     | 0        | 0            | 8.69     | 0        | 0            |
| Suspended substances, mg/dm³                  | 0.6   | 120      | 23724    | 197.7        | 99.5     | 4241     | 35.34        | 97.2         |
| Dry residue, mg/dm³                           | 0.70  | 700      | 565      | 0            | 0        | 1210     | 1.73         | 42.1         |
| Chlorides, mg/dm³                             | 0.118 | 118      | 34       | 0            | 0        | 27       | 0.0          | 0            |
| Sulfates, mg/dm³                              | 0.160 | 160      | 91       | 0            | 0        | 174      | 1.09         | 8.0          |
| Ammonium ion, mg/dm³                          | 0.65  | 6.5      | 5.5      | 0            | 0        | 3.01     | 0.47         | 0            |
| Nitrite ion, mg/dm³                           | 0.66  | none     | 0        | 0            | 0        | 0.90     | 1.36         | 26.7         |
| Nitrate ion, mg/dm³                           | 13.29 | 2.34     | 0        | 0            | 0        | 2.60     | 0            | 0            |
| Phosphates on Phosphorus, mg/dm³              | 1.8   | 0.13     | 0        | 0            | 0        | 1.96     | 1.09         | 8.1          |
| Iron Total, mg/dm³                            | 0.6   | 41.0     | 68.4     | 98.5         | 29.61    | 49.34    | 98.0         |              |
| Petroleum products, mg/dm³                    | 0.2   | 4.3      | 21.6     | 95.4         | 16.82    | 84.12    | 98.8         |              |
| Sulfides, mg/dm³                              | 0.3   | 0.22     | 0        | 0            | 0        | none     | 0            | 0            |
| Surface-active agents (anion-active), mg/dm³  | 0.25  | 6.65     | 26.6     | 96.2         | 4.15     | 16.59    | 94.0         |              |
| Aluminium, mg/dm³                             | 0.15  | 0.04     | 0        | 0            | none     | 0        | 0            |              |
| Copper, mg/dm³                                | 0.017 | 1.547    | 91.0     | 98.9         | 0.67     | 39.42    | 97.5         |              |
| Zinc, mg/dm³                                  | 0.05  | 0.31     | 6.2      | 83.9         | 1.09     | 21.80    | 95.4         |              |
| Nickel, mg/dm³                                | 0.06  | 0.02     | 0        | 0            | 0.04     | 0        | 0            |              |
| Cadmium, mg/dm³                               | none  | 0.26     | 0.3      | 100          | 1.14     | 1.14     | 100.0        |              |
| Lead, mg/dm³                                  | 0.014 | 0.147    | 10.5     | 90.5         | 1.10     | 78.33    | 98.7         |              |
| Chromium III, mg/dm³                          | none  | none     | 0        | 0            | none     | 0        | 0            |              |
| Chromium VI, mg/dm³                           | none  | none     | 0        | 0            | none     | 0        | 0            |              |
| COD mgO₂/dm³                                  | 800   | 785.7    | 0        | 0            | 328      | 0        | 0            |              |
| Hydrogen parameter, pH                        | 6.5-8.5 | 7.28     | 0        | 0            | 7.03     | 0        | 0            |              |
| Suspended substances, mg/dm³                  | 0.6   | 120      | 323      | 2.7          | 62.9     | 11727    | 97.7         | 99.0         |
| Dry residue, mg/dm³                           | 0.70  | 700      | 349      | 0            | 0        | 453      | 0            | 0            |
| Chlorides, mg/dm³                             | 0.118 | 118      | 32.45    | 0            | 0        | 35.99    | 0            | 0            |
| Sulfates, mg/dm³                              | 0.160 | 160      | 82.57    | 0            | 0        | 51.45    | 0            | 0            |
| Ammonium ion, mg/dm³                          | 0.65  | 0.2      | 0        | 0            | 3.55     | 0        | 0            |              |
| Nitrite ion, mg/dm³                           | 0.66  | 0.04     | 0        | 0            | none     | 0        | 0            |              |
| Nitrate ion, mg/dm³                           | 13.29 | 2.6      | 0        | 0            | 1.82     | 0        | 0            |              |
| Phosphates on Phosphorus, mg/dm³              | 1.8   | 0.008    | 0        | 0            | 0.47     | 0        | 0            |              |
| Iron Total, mg/dm³                            | 0.6   | 0.512    | 8.5      | 88.3         | 45.82    | 76.4     | 98.7         |              |
| Petroleum products, mg/dm³                    | 0.2   | 1.00     | 5.0      | 80.1         | 29.9     | 149.7    | 99.3         |              |
| Sulfides, mg/dm³                              | 0.3   | none     | 0        | 0            | 0.21     | 0        | 0            |              |
| Surface-active agents (anion-active), mg/dm³  | 0.25  | 0.01     | 0        | 0            | 1.78     | 7.1      | 86.0         |              |
| Aluminium, mg/dm³                             | 0.15  | traces   | 0        | 0            | 0.03     | 0        | 0            |              |
| Copper, mg/dm³                                | 0.017 | 0.005    | 0        | 0            | 1.699    | 99.9     | 99.0         |              |
| Zinc, mg/dm³                                  | 0.05  | 0.031    | 0        | 0            | 0.91     | 18.3     | 94.5         |              |
| Nickel, mg/dm³                                | 0.06  | none     | 0        | 0            | none     | 0        | 0            |              |
| Cadmium, mg/dm³                               | none  | 0.265    | 0.3      | 100          | 1.51     | 1.5      | 100          |              |
| Lead, mg/dm³                                  | 0.014 | none     | 0        | 0            | 0.075    | 5.4      | 81.3         |              |
| Chromium III, mg/dm³                          | none  | none     | 0        | 0            | none     | 0        | 0            |              |
| Chromium VI, mg/dm³                           | none  | traces   | 0        | 0            | 0.005    | 0        | 100          |              |
| COD mgO₂/dm³                                  | 800   | 172.5    | 0        | 0            | 691.6    | 0        | 0            |              |

Notes: 1. MAC values are given for effluents discharge into municipal sewage. 2. E – Excess over MAC, times. 3. D – Required degree of purification, %, up to MAC.
2. Car-wash wastewater is mostly polluted with suspended substances and surfactants. Its chemical composition is similar to wastewater of the assembly site and the anti-corrosion treatment workshop. The peculiarity of the assembly site drainage is its increased salt content (its dry residue exceeds MAC by 1.7 times), as well as the presence of excess MAC of phosphates.

3. Paint-and-varnish department (PVD) wastewater is characterized by a comparatively small MAC excess (maximum 8.5 times on the iron) according to only four parameters (suspended substances, iron, petroleum products, cadmium). It is also characterized by small concentrations of surfactants, heavy metals and the minimal content of oil products out of all effluents under analysis.

4. A common feature of the effluents in question is the presence of cadmium. The norms of cadmium correspond to a zero level in all regulations and norms. Cadmium is regularly found in PVD wastewater. Its amount corresponds to that of car-wash wastewater. Other heavy metals concentrations in this drainage are minimal and do not exceed established MAC.

This analysis clearly shows the diversity of CSS wastewater composition. This diversity makes it difficult to achieve MAC standards for the discharge into the municipal sewer network. Besides, 94.3 to 95.8% of all CSS wastewater drains from the car-wash area. That is why the researchers decided to make a circulating water supply system only for the car-wash facilities and for local sewage treatment plants, such as for "Agregatka", "Anticor" and PVD workshops. For that reason, the authors have chosen the car-wash workshop drainage for further research and tried to determine best possible purification methods of its wastewater. Several standard methods were used at the first stage of purification: sedimentation, coagulation with the use of chemical treating agents and electroflotocoagulation.

3. Main Research

The investigation of the sedimentation process was carried out in six Lisenko vessels, their capacity being 500 ml each. After careful mixing, a sample of water was taken out of the total volume to determine its optical density \(D_o\) by using a blue filter of photoelectric colorimeter. Then, the remaining source water was re-mixed and poured into the vessels. The beginning of the sedimentation process in each vessel was carefully recorded, \(T_o\). After 120 minutes sedimentation, a sample of water was taken from each vessel. The value of the optical density \(D_i\) was determined for each sample. The sediment amount \(W_{oc}\) was fixed visually [17]. It was found that after non-reagent sedimentation, the clarification effect for this wastewater did not exceed 18%. The sediments consisted of fine sand and finely-dispersed suspended solids.

At the next stage, coagulation with the help of aluminum sulfate and aqua-aurate 30 was carried out in eight Lisenko vessels, their capacity being 1000 ml each. The method of mathematical planning experiments was applied at this stage [15]. Wastewater samples of 8 dm\(^3\) were taken for each type of coagulant during these experiments. After careful mixing with the help of a magnetic mixer, a sample of water was taken out of the total volume to determine its optical density \(D_o\) by using the same photoelectric colorimeter. After re-mixing, the remaining source water was poured into the vessels and the necessary amount of \(A_c\) coagulant was added to the samples. Then the contents of the cylinders was quickly stirred for 1 minute. After that, the cylinders were left to stay still for the appropriate length of time, \(T_s\). After the specified time (see Table 2) of sedimentation \(T_s\), the samples of water were selected from each vessel. The value of optical density \(D_i\) was determined for each sample [17]. It was a random experimental procedure.

It was found that the amount of Aqua-aurate (AA) necessary to achieve a certain degree of water clarification is three times less than the amount of \(Al_2(SO_4)_3\). The kinetics of the processes presented in the form of regression equations in implicit form (1) and (2) showed a greater efficiency of AA in the centre of the planning matrix. In both cases, the \(A_c\) has 12-60 times more influence on the process of water clarification than the duration of its sedimentation \(T_s\).

\[
D_{Al_2(SO_4)_3} = 46.0 + 30.9x_1 + 0.52x_2 - 0.28x_1x_2
\]  

(1)
The fallen sediment took up the form of low-density flocculates.

Electroflotocoagulation with the use of aluminum and steel electrodes was carried out in eight dimensional vertical chemical cylinders, with a capacity of 1000 ml each.

Wastewater samples of 8 dm³ were taken for each type of electrode during these experiments. After careful mixing, a sample of water was taken out of the total volume to determine its optical density $D_o$ by using the same photoelectric colorimeter. After re-mixing, the remaining source water was poured into the vessels. Then the researchers dipped the electrodes into the vessels and set the desired force of a direct current. To prevent the passivation of electrodes, the polarity on the electrodes was changed before the start of each test. Alloys of grades D16A and St. 3 were used as electrodes.

Table 2. Results of wastewater purification by reagent sedimentation.

| Experiments | $X_0$ | Plan | Values of independent factors | State variable | $D_i$, % |
|-------------|-------|------|--------------------------------|----------------|---------|
|             | $X_1$ | $X_2$ | $X_1X_2$ | $A_c$, mg/l | $T_s$, min | $D_o$ | $D_1$ | $D_2$ | $D_{av}$ |
| 1           | +     | +     | +    | 450 | 30 | 28.82 | 7.82 | 5.4 | 6.61 | 77.06 |
| 2           | +     | -     | +    | 50  | 30 | 28.82 | 24.1 | 24.28 | 24.19 | 16.07 |
| 3           | +     | +     | -    | 450 | 10 | 28.82 | 8.28 | 5.22 | 6.75 | 76.58 |
| 4           | +     | -     | +    | 50  | 10 | 28.82 | 24.88 | 24.42 | 24.65 | 14.47 |

Table 3 demonstrates the results of these studies in the form of equations (3) and (4).

$$D_{Al} = 57.1 + 24.4x_1 + 2.0x_2 - 1.9x_1x_2$$

(2)

$$D_{Fe} = 59.0 + 6.1x_1 + 25.9x_2 - 4.2x_1x_2$$

(3)

$$D_{Fe} = 73.8 + 5.9x_1 + 16.8x_2 - 4.0x_1x_2$$

(4)

After the specified time $T_s$ (see Table 3), the system was consistently transferred to flocculation and sedimentation modes (with 10-minute duration of each stage). Then, a sample of water was selected from each vessel and the value of the optical density $D_i$ was determined for each sample [17].

Table 3. Results of wastewater purification by reagent sedimentation.

| Experiments | $X_0$ | Plan | Values of independent factors | State variable | $D_i$, % |
|-------------|-------|------|--------------------------------|----------------|---------|
|             | $X_1$ | $X_2$ | $X_1X_2$ | $T_s$, s | $i$, A/m² | $D_o$ | $D_1$ | $D_2$ | $D_{av}$ |
| 1           | +     | +     | +    | 600 | 138.89 | 24.30 | 2.53 | 2.37 | 2.45 | 89.92 |
| 2           | +     | -     | +    | 300 | 138.89 | 24.30 | 4.30 | 5.48 | 4.89 | 79.88 |
| 3           | +     | +     | -    | 600 | 27.78  | 24.30 | 13.58 | 15.46 | 14.52 | 40.25 |
| 4           | +     | -     | +    | 300 | 27.78  | 24.30 | 17.46 | 18.48 | 17.97 | 26.05 |

$$D_{Fe} = 12.05 + 13.63 + 12.84 + 72.16$$

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It is established, that under other equal conditions the degree of drainage clarification by electroflotocoagulation is approximately identical, and the cost of electric power is 1.13 times higher with steel electrodes than that with aluminium electrodes. The kinetics of the clarification process was similar. When aluminum electrodes were used, the significance of the factor known as "current density on the electrodes" \( (i, \text{A/m}^2) \) was 4.2 times higher than the factor known as "duration of electrical treatment" \( (T_s, \text{s}) \). The same factor value for steel electrodes is 2.8 times. Thus, electroflotocoagulation, as well as reagent coagulation with subsequent sedimentation, can be successfully applied for this drainage purification at the first stage of treatment, with clarification efficiency from 87 to 92%. However, after treatment is required in order to return this wastewater to the circulating system of the enterprise.

At the second stage of purification, the researchers used filtering through two natural sorbent agents. These agents are vermiculite and brucite. Vermiculite is a mineral with an expanding structure, which belongs to layered and layered-band alumo-ferro-magnesium silicates [16]. Brucite \( \text{Mg(OH)}_2 \) is a natural crystalline magnesium hydroxide containing the maximum amount of magnesium possible in natural materials (up to 69% \( \text{MgO} \)) [18]. These sorbent agents are characterized by wide availability and cheapness.

At the first stage, the researchers chose the most simple and cheap method of coagulation involving the use of Aqua-aurate and Aluminum sulfate. Coagulation was carried out in a 50-litre capacitive chamber. The source water was taken from the flow-equalization basin of CSS wash-water. After adding the previously obtained optimal amount of coagulant (for \( \text{Al}_2\text{O}_3 \), 150 mg/dm3 for AA and 450 mg/dm3 for \( \text{Al}_2(\text{SO}_4)_3 \), respectively)/ The content of the chamber was intensively mixed during two minutes. Then it was left to stay for 30 minutes. The drainage clarified with sedimentation was filtered at \( v_f = 10.0 \text{ m/h} \) through two columns with vermiculite and brucite loading.

The clarifying effect was assessed by changing of suspended substances concentration. Paper [19-21] perform the cluster analysis to define the hierarchical classification of 21 water quality indices. According to this analysis results, the "suspended substances" parameter is the defining (leading) dominant for the "oil products" parameter. It means, it is possible to assess the quality of water purification from suspended substances and oil products only by the change in the "suspended substances" parameter.

The results were processed by methods of mathematical statistics at 0.05 level of importance according to the methodology introduced in Paper 3 [15]. They are shown in Table 4.

The analysis of the obtained results shows that the water clarification effect was very high. Comparing two kinds of filtering loads shows that vermiculite is more preferable and effective because its purification effect is more apparent than that of brucite. Besides, vermiculite partially removes the smell of the wastewater drainage. In addition, the use of AA allows to significantly reduce the salt load on reservoirs and watercourses and keep the pH value within required MAC.

Table 4. Results of drainage purification after car-washing by treating agents sedimentation and subsequent filtration.

| Treating agent (its amount, mg/dm³) | Concentration of suspended substances, mg/dm³, in the source water | after sedimentation *\(^{b}\) | After filtering through brucite*\(^{f}\) | vermiculite *\(^{f}\) |
|------------------------------------|---------------------------------------------------------------|---------------------------------|---------------------------------|---------------------|
| Aqua-aurate (150)                  | 2012.0 ± 98.3                                                 | 76.4 ± 12.6                     | 26.2 ± 5.1                      | 4.0 ± 0.7           |
| pH                                 | 8.45                                                         | 96.2                            | 98.7                            | 99.8                |
| \( \text{Al}_2(\text{SO}_4)_3 \) (450) | 1953.1 ± 73.5                                                 | 76.2 ± 15.1                     | 27.3 ± 4.9                      | 5.9 ± 1.1           |
| pH                                 | 8.98                                                         | 96.1                            | 98.6                            | 99.7                |

*\(^{b}\) in the numerator – mg/dm³, in the denominator – the effect of purification, %
4. Conclusion
The research yielded the following conclusions:

1. To prepare wastewater drainage for its return into the system of circulation water supply system of car service stations, their 2-stage purification consisting of treating agents sedimentation and filtration is required. Aqua-aurate of 150 mg/dm$^3$ amount is suggested as a treating agent in this process and vermiculite is recommended as a filter loading. The use of AA allows to significantly reduce the salt load on reservoirs and watercourses and keep the pH value within required MAC.

2. With wastewater discharge up to 1000 m$^3$/day, both electroflotocoagulation and reagent coagulation with the following sedimentation, can be successfully used at the first stage of this wastewater drainage purification.

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