Waste Water Purification with Coagulants after Linoleum Colouration

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Abstract. The paper focuses on the possibility of wastewater treatment which is produced when printing cylinders of linoleum production are being washed out with coagulants. Literature review shows that coagulation is the most appropriate method for the treatment of wastewater contaminated with acrylic paint. Studies on wastewater coagulation with iron chloride, iron sulfate and aluminium sulfate made it possible to determine the optimal dose of coagulant for purifying wastewater from acrylic paint. The conducted research made it possible to design a technological scheme of wastewater treatment from washing out of printing cylinders of linoleum production, and also to offer recommendations on purified water disposal.

1. Introduction
Linoleum patterning is carried out by rolling printing cylinders over its surface. It is usually done with acrylic paints which are water-dispersive paints on the basis of polyacrylates serving as film-formers and colourants. In general, acrylic paints are microheterogeneous colloid systems. These systems are highly concentrated suspensions with a film-former or its water solution as the dispersion medium, and with colourants and fillers as the dispersion phase. Colourants are inherently inert and hydrophobic, they do not dissolve in water and are not dispersed. Colloid-dispersed systems are aggregatively unstable. When subject to a gravity force, they coagulate. As their particles become larger, colloid-dispersed systems begin to lose their sedimentation stability which is accompanied by sediment precipitation. Therefore, surface-active substances (surfactants) [1-5] are used to stabilize colourants dispersion.

2. Methodology
Wastewater formed as a result of printing cylinders washing out is a dilute acrylic paint with its original properties.

Paper [6] gives a brief analysis of possible methods of wastewater treatment from linoleum colouration and points outs those methods requiring further research [7, 8].
This study deals with water purification which is produced when printing cylinders of linoleum production are being washed out with electrolyte coagulation. Iron chloride, iron sulfate and aluminium sulfate were used as coagulants. To create optimum conditions for coagulation, the researchers used such alkaline agents as sodium hydrate and caustic lime. The dose of coagulant was determined experimentally. The dose of the alkalizing agent depended on the need to ensure optimal pH value necessary for the metals added into the treated water to form insoluble compounds [9, 10].
3. Experimental Part

The contaminated water under analysis was poured into vessels (cylinders) with 500 ml capacity. Further, the coagulant with a fixed dose was also added into the water. After adding the coagulant, the solution was quickly stirred for 30 sec. Then the vessels were left alone for 24 hours, and the researchers observed the formation and deposition of flocculates. After every test, a water sample was taken from the upper layer of each vessel without stirring up the sediment.

3.1. Experiment 1

20% solution of iron chloride (FECl₃) was used as a coagulant. 20% pH factor of iron chloride solution was 1.2 pH units. The coagulant doses were taken as follows: 0.5, 1, 2, 4, 6 g/l. To ensure the optimum pH value, 10% sodium hydrate (NaOH) was added to the water under investigation during coagulation of pollutants.

Figures 1 and 2 show the sample of analyzed wastewater after 1 and 24 hours of settling after iron chloride dose of 2.0 g/l was added. Table 1 shows the results of laboratory studies of wastewater settling within 24 hours after iron chloride treatment.

3.2. Experiment 2

20% solution of iron sulfate (Fe (SO₄) was used as a coagulant. 20% pH factor of iron sulfate solution was 4.0 pH units. The coagulant doses were taken as follows: 0.5, 1, 2, 4, 6 g/l. To ensure the optimum pH value, 5% lime milk (Ca(OH)₂) was added to the water under investigation during coagulation of pollutants.

Figures 3 and 4 show the sample of analyzed wastewater after 1 and 24 hours of sedimentation after iron sulfate dose of 2.0 g/l was added. Table 2 shows the results of laboratory studies of wastewater settling within 24 hours after iron sulfate treatment.

Table 1. Research results of wastewater treatment by 20% solution of iron chloride.

| Dose of FeCl₃, mg/l | Residual concentration of chlorides Cl⁻, mg/l | Residual concentration of iron Fe³⁺, mg/l |
|-------------------|---------------------------------------------|----------------------------------------|
| 0                 | 2906                                        | 0.0                                    |
| 500               | 2978                                        | 4.44                                   |
| 1000              | 3080                                        | 9.24                                   |
| 2000              | 3051                                        | 53.3                                   |
| 4000              | 3254                                        | 80.0                                   |
| 6000              | 5429                                        | 147.6                                  |
**Figure 1.** 1-hour retention time.

**Figure 2.** 24-hour retention time.

**Figure 3.** 1-hour retention time.

**Figure 4.** 24-hour retention time.
Table 2. Research results of wastewater treatment by 20% solution of iron sulfate.

| Dose of FeSO₄, mg/l | Dose Ca(OH)₂, mg/l | Residual concentration of chlorides Cl⁻, mg/l | Residual concentration of sulfates SO₄²⁻, mg/l | Residual concentration of iron Fe²⁺, mg/l | Dry residue, mg/l |
|---------------------|--------------------|---------------------------------------------|---------------------------------------------|------------------------------------------|-----------------|
| 0                   | 3559.9             |                                             |                                             | 24.4                                     | 16176           |
| 500                 | 250                | –                                           | –                                           | 15.5                                     | 15204           |
| 1000                | 250                | –                                           | –                                           | 15.5                                     | 15204           |
| 2000                | 500                | 3240.2                                      | 2906                                        | 0.31                                     | 14522           |
| 4000                | 500                | 3036.8                                      | 2976                                        | 6.44                                     | 12926           |
| 6000                | 500                | 3574.4                                      | 3196                                        | 116.5                                    | 16574           |

3.3. Experiment 3

20% solution of aluminium sulfate (Al₂(SO₄)₃) was used as a coagulant. 20% pH factor of aluminium sulfate solution was 3.0 pH units. The coagulant doses were taken as follows: 1, 2, 3, 4, 6 g/l. To ensure the optimum pH value, 10% sodium hydrate (NaOH) was added to the water under investigation during coagulation of pollutants.

Figures 5 and 6 show the sample of analyzed wastewater after 1 and 24 hours of sedimentation after aluminium sulfate dose of 2.0 g/l was added. Table 3 shows the results of laboratory studies of wastewater settling within 24 hours after aluminium sulfate treatment.

Figure 5. 1-hour retention time.

Figure 6. 24-hour retention time.

4. Results

The researches revealed that the optimum dose for all coagulants is 2.0 g/l. The composition of treated wastewater after using the coagulants described above is as follows: dry residue – 13000 mg/l, chlorides – 4000 mg/l, sulfates – 2000 mg/l. Besides, the research helped develop the technological scheme of a wastewater treatment plant for purifying wastewater which is produced when printing cylinders of linoleum production are being wash out (Figure 7).
Table 3. Research results of wastewater treatment by 20% solution of aluminium sulfate.

| Al₂(SO₄)₃ dose, mg/l | Hydrogen Index, unit pH | Residual concentration of chlorides Cl⁻, mg/l | Residual concentration of sulfates SO₄²⁻, mg/l | Residual concentration of aluminium Al³⁺, mg/l | Dry residue, mg/l |
|----------------------|-------------------------|---------------------------------------------|----------------------------------------------|---------------------------------------------|------------------|
| 500                  | 3.9                     | 2900                                        | 2084                                         | 87                                          | 13240            |
| 1000                 | 3.78                    | 2900                                        | 2196                                         | 93                                          | 14386            |
| 2000                 | 4.05                    | 2755.0                                     | 2210.0                                       | –                                           | 13402            |
| 3000                 | 6.91                    | –                                           | –                                            | 4.4                                         | 12530            |
| 4000                 | 3.9                     | 3045.0                                     | 2342                                         | –                                           | 13584            |
| 6000                 | 3.74                    | 10947.5                                    | 5445.5                                       | –                                           | –                |

Figure 7. Technological scheme of a wastewater treatment plant for purifying wastewater after washing out of printing cylinders: P1 – storage basin, P2 – reactor, P3 – a reservoir for dilution of purified sewage, B1 – coagulant service tank, B2 – alkaline service tank, B3 – flocculant service tank, F1 – filter press, H1, H2, H3 – pumps.
Wastewater after treatment from acrylic paint components does not meet either the requirements of the household sewage system discharge [11], nor the Federal Service for Supervision of Natural Resource Usage Regulations for the discharge into the waterbodies according to a number of indicators (chlorides, sulfates, dry residue) (see Table 4).

**Table 4. Conditions for wastewater disposal into household sewage systems and into waterbodies.**

| Marker                  | Unit of measurement | Standards for the discharge of contaminants into household sewage system | The norm for the discharge of contaminants into waterbodies | Permissible content of contaminants in purified washwater |
|-------------------------|---------------------|-------------------------------------------------------------------------|-----------------------------------------------------------|--------------------------------------------------------|
| Chlorides               | mg/dm³              | 178.9                                                                   | 300                                                       | 4000                                                   |
| Sulphates               | mg/dm³              | 100                                                                     | 100                                                       | 2000                                                   |
| Phenol                  | mg/dm³              | none                                                                    | 0.001                                                     | n/a                                                   |
| Petroleum products      | mg/dm³              | 0.03                                                                    | 0.05                                                     | n/a                                                   |
| Synthetic surfactants   | mg/dm³              | 0.16                                                                    | 0.1                                                      | n/a                                                   |
| Suspended materials     | mg/dm³              | 72                                                                      | 13.95                                                    | n/a                                                   |
| BOD<sub>total</sub>     | mgO<sub>2</sub>/dm³ | 50.0                                                                    | 3.0                                                      | n/a                                                   |
| COD<sub>mgO<sub>2</sub>/dm³</sub> |            | 15                                                                     | n/a                                                      |                                                       |
| Dry residue             | mg/dm³              | 1000                                                                    | 1000                                                     | 13000                                                  |

It is possible to meet the normative requirements to the quality of purified washwater by way of its dilution with domestic sewage of enterprises or by purified superficial sewage waters (rain and snow-melt). The rain and snow-melt water can be used for production needs or disposed into a waterbody in case of its overflow (see Table 5).

**Table 5. Wastewater qualitative composition.**

| Marker       | Unit of measurement | Domestic sewage | Treated surface waste water | Purified washwater |
|--------------|---------------------|-----------------|-----------------------------|--------------------|
| Chlorides    | mg/dm³              | 130             | 52                          | 4000               |
| Sulphates    | mg/dm³              | 270             | 41                          | 2000               |
| Dry residue  | mg/dm³              | 800             | 233                         | 13000              |

The concentration of the component after mixing two water streams or the amount of water necessary for the specified value of concentration can be determined by the formula:

\[ C_1 \cdot Q_1 + C_2 \cdot Q_2 = C_3 \cdot Q_3 \]

where \( C_1, C_2, C_3 \) are component concentrations in purified washwater, in water used for dilution; in the merged stream, respectively; 
\( Q_1, Q_2, Q_3 \) are consumption of purified washwater; in water used for dilution; in the merged stream, respectively.

The calculations were made for the company located in the city of Otradniy, Samara region, for the following source data:
- consumption of treated wastewater is 40 m³/month, 1.82 m³/day;
- consumption of domestic sewage is 1500 m³/month, 68 m³/day;
- consumption of surface wastewater is 92547 m³/year, 253.6 m³/day.
5. Conclusions
The research shows that:

- It is not possible to meet the requirements for wastewater disposal into domestic sewage by mixing it only with domestic sewage water according to three indicators (chlorides, sulfates, dry residues). Additional dilution of this wastewater with treated surface wastewater is required;
- The requirements for wastewater disposal into domestic sewage according to chlorides and dry residue indicators can be met when adding to it 630 m$^3$/month, 7560 m$^3$/year purified surface wastewater;
- The requirements for wastewater disposal into domestic sewage according to chlorides and dry residue indicators can be met when adding to it 1290 m$^3$/month, 15480 m$^3$/year purified surface wastewater.

6. References
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