Contents lists available at Science-Gate

International Journal of Advanced and Applied Sciences

Journal homepage: http://www.science-gate.com/IJAAS.html

Wastewater treatment, relations and inspiration

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A R T I C L E I N F O

Article history:
Received 27 July 2015
Received in revised form
2 October 2015
Accepted 7 October 2015

Keywords:
Wastewater
Treatment
Inspiration

A B S T R A C T

The suggested technology and extractant in this paper allow extracting up to 99.8% of weight. It was proven that the average drop size reduces when the breakup frequency is increased, which plays a significant role for the process implementation. The coalescence frequency in a fluid medium was proven to depend on drop concentration, stirrer revolution speed and medium viscosity. The model of the immiscible liquid phases' disengagement process was composed. The paper provides equations for calculating the drop breakup and coalescence frequency, the interphase film, defines the experimental and estimated values of the absorbed agent concentration, reveals the dependence of isopropyl ether volume flow rate on organic solvent content. The paper suggests conditions for dispersed system diffusion in a gravitational field. The role of the Marangoni effect during phase coalescence, breakup and disengagement is studied in the given paper. The drop distribution over the intermediate layer height was proven to be simpler for small Peclet number values (Pe<<1).

1. Introduction

Many wastewaters are contaminated by substances that are toxic to both the environment and people. Such substances include paint-and-varnish manufacturers' organic solvents. In order to achieve high results, paint-and-varnish manufacturers use electrolyte compounds containing organic solvents that are highly and slightly soluble in water, such as butyl glycol, phenyl isopropanol, acetic acid and acetyl acetone. As of today, no single existing method of wastewater treatment with a view to removing said contaminants allows purifying water to the maximum permissible concentration (MPC) from the environmental and economic perspective.

Wastewater treatment in order to remove hydrocarbon is currently performed by mechanical, physical-and-chemical, chemical and biological methods. Such methods have a number of considerable setbacks (Capola and Roberto, 2015).

Chemical methods imply introducing chemical reagents into the treated water (Corvalan, 2004; Fiehn, 1994; Coffelt, 2009). The occurring chemical reactions can form substances that are even more toxic that the initial ones.

Mechanical treatment methods remove only floating hydrocarbons (Veytser, 1988). Emulsified and dissolved hydrocarbons are not extracted; therefore, such treatment is inefficient.

Flotation treatment implies introducing into the treated water chemical reagents, which facilitate emulsified particle growth. Hence, the treated water is contaminated.

Biological oxidation is applicable only with a low contaminant concentration, under strict observance of temperature and pH conditions (Rao, 2009).

Wastewater sorption treatment allows reaching required hygienic standards (Rao, 2009). This method is mostly used at the advanced treatment stage, due to high sorbent cost.

Proceeding from the above, the development of high-efficiency and cheap methods of treating wastewater in order to remove hydrocarbons is relevant for both the economy and ecology.

In order to solve the problem, an extraction of paint-and-varnish manufacturers' wastewater in an extraction column was carried out with a view to removing butyl glycol, phenyl isopropanol and acetic acid. Isopropyl ether was used as an extract ant (Gasanov, 2011).

The designed method of treating paint-and-varnish manufacturers' wastewater by liquid-phase extraction allows achieving a high purification level – 99.8%. At that, the pollution agent content in wastewater is at the MPC level.

2. Materials and methods

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The objective of the given research is to develop an environmentally and economically efficient waste-free treatment technology of paint-and-varnish manufacturers' wastewater and mathematically describe the process of liquid-phase extraction by isopropyl ether in a stirring extractor.

The paper presents research results on the development of a waste-free, environmentally friendly technology of recovering organic products from paint-and-varnish manufacturers' wastewater by liquid-phase-extracting them from the aqueous solution with a subsequent reintroduction of the solvent, agents and treated water into the process.

Numerous extract ants were tested for separating the abovementioned agents – ethers, liquid aliphatic and aromatic hydrocarbons. Isopropyl ether was chosen based on physical-and-chemical properties: component solubility degree, selectivity, efficiency, distribution factor, capacity, recoverability, density, interphase tension, reactivity, stability, viscosity and toxicity (Gasanov, 2012; Hamid, 2012; Gasanov, 2014; Gasanov, 2014a; Gasanov, 2014b; Gasanov, 2014).

Experimental researches of liquid-phase extraction by isopropyl ether were carried out on a wastewater sample containing butyl glycol, phenyl isopropanol, acetic acid and acetyl acetone. The ratio is presented in Table 1(Gasanov, 2014b; Dytnerskiy, 1995; Hesketh, 1991).

Table 1: Wastewater content

Wastewater content	Consumption		Concentration		
	g/hour	mole/hour	% weight	g/l	mole/l
Butyl glycol	30.6	0.339	1.02	10.2	0.113
Phenyl isopropanol	19.5	0.143	0.65	6.5	0.048
Acetic acid	26.1	0.435	0.87	8.7	0.145
Acetilacetone	3.6	0.036	0.12	1.2	0.012
Water	2920.2	162.233	97.34	973.4	54.080
Total	3000.0	163.186	100.00	1000.0	54.386

Experiments were conducted with a view to finding the optimal volume ratio of isopropyl ether and wastewater. By means of numerous experiments, the optimal extract ant consumption was determined, including the volume ratio of wastewater and isopropyl ether. Consumption of wastewater and isopropyl ether was 3 l/hour and 200 ml/hour, respectively. The wastewater to isopropyl ether volume ratio was 15:1.

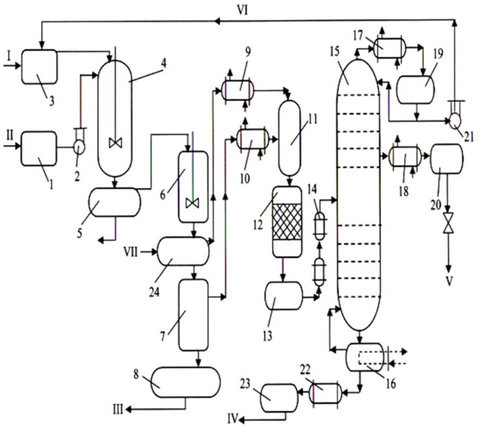
When choosing extract ants, it was necessary to take account of up to 19 various requirements to the equipment. Taking into consideration the productivity, liquids' physical properties, mass transfer into the water phase, low flow rate, emulsification tendency, limited working area, manageability and low capital and operation expenses, the author chose the stirring extractor.

Extraction was carried out at the temperature of 20°C and under atmospheric pressure. The diameters of the extractor and stirrer are $D = 0.12$ m, $d_m = 0.08$ m, respectively.

3. Results

The full flow sheet for extracting water-emulsion organic solvents and admixtures from wastewater being generated due to obtainment of anticorrosive protection film materials at paint manufacturers is presented in Fig. 1.

It is worth noting that the extractor is equipped with a stirrer in order to increase the contact interphase area. During stirring, the drop breakup frequency ω is proportional to the stirrer revolution speed W and diameter D, $\omega \sim W^{1/2} D^{1/3}$. Coalescence frequency in a fluid medium depends on drop concentration φ_o and medium viscosity v_C as $\omega \sim \varphi_o D \left(W^3 / v_C \right)^{1/2}$. Drop coalescence is energy-efficient so long as two layers of immiscible liquids are formed, which facilitates efficient phase disengagement. The main role in the given process is played by drop sizes, which depend on stirring conditions and medium physical-and-chemical properties (density, surface tension, dissipation energy density) (Blanchette, 2009; Ceylan, 2003; Marra, 1991).



1 – wastewater container; 2, 21 – pumps; 3 – extract ant container; 4 – extractor; 5 – sedimentation container; 6 – separation funnel; 7 – evaporator; 8 – treated wastewater container; 9, 10, 17, 18, 22 – tubular coolers; 11 – collector; 12 – dehydration apparatus; 13 – extract container; 14 – heat transfer units; 15 – distillation column; 16 – evaporator-re boiler; 19, 20, 23 – containers; 24 – settler. Flows: I – isopropyl ether; II – contaminated wastewater; III – purified water; IV – organic solvent mixture; V – organic solvent and isopropyl ether mixture; VI – isopropyl ether; VII – demulsifying agent.

Fig. 1: Flow sheet of wastewater extraction treatment with a view to removing hydrophobic organic solvents:

An important role in extraction, coalescence, breakup and disengagement is played by the Marangoni effect, which consists in the formation of an additional convective current on the drop and interphase surface due to different values of surface tension coefficients and isopropyl ether (Mao, 2004). Theoretical researches showed that the presence of the Marangoni effect somewhat facilitates emulsion stabilization, which leads to the reduction of breakup and extraction speed. The Marangoni effect facilitates temporary stabilization of the interphase film, since in any spot, where the film becomes thinner due to external forces' effect, a local surface tension increase occurs, which counteracts coalescence, drop growth and phase disengagement.

During liquid extraction on the interphase film surface, as with any mass transfer process, the following boundary condition in satisfied

$$D\frac{\partial c}{\partial r}\Big|_{r-\delta} = \beta(c-c_0) \qquad (1)$$

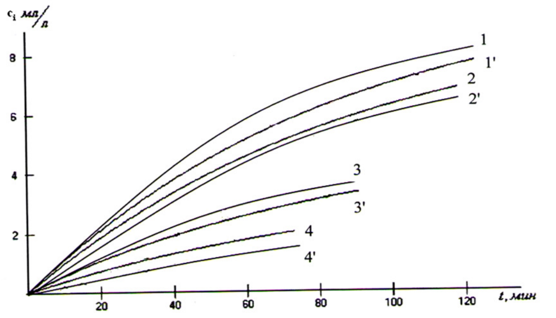
where *D* is the molecular diffusion coefficient, *β* is the mass transfer coefficient, *r* is the interphase layer thickness, c is the absorbed substance concentration, c_0 is the balanced concentration between phases, *δ* is the interphase layer thickness, which is proportional to $\delta \sim \left(\frac{aD}{V}\right)^{1/2}$, *a* is the drop size, V is the flow rate on the drop surface. Assuming that in this equation for small interphase film thickness $dr = Vdt$, the equation can be written in the following form:

$$\frac{\partial c}{\partial t} = K(c-c_0). \quad c\big|_{t=o} = c_0 \qquad (2)$$

Where $K = \frac{\beta V}{D}$ the extraction kinetic coefficient, t is the extraction time. The expression (2) is a kinetic equation for extraction processes. It characterizes the change rate of the absorbed substance concentration in time. With a constant K coefficient value, the solution of equation (2) can be written in the following form:

$$c(t) = c_0\left[1-\exp(-Kt)\right] \qquad (3)$$

In order to study the extraction kinetics of hydrophobic organic solvents and component substances with the application of isopropyl ether as an extract ant, a number of experiments were conducted in stirring machines at a temperature of 20°C during 0.1-1.5 hours. The results of experimental researches (3) are presented in Fig. 2.



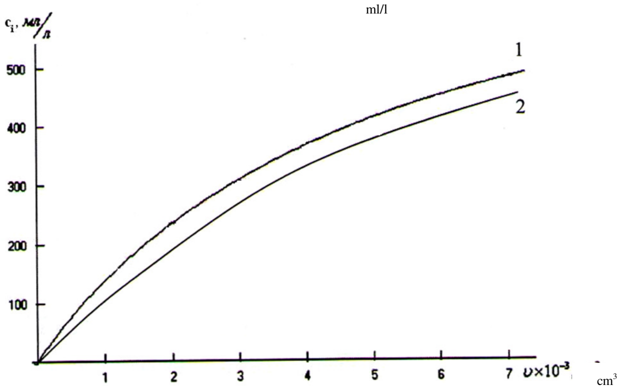
1, 2, 3 and 4 are experimental concentration values at 3.67; 5.04; 9.32 and 10.19 ml/l, respectively
1', 2', 3' and 4' are estimated concentration values at 3.67; 5.04; 9.32 and 10.19 ml/l, respectively

Fig. 2: Comparison of experimental and estimated concentration values of the component absorbed from wastewater in time under various values of its initial concentration $^{ml}/_{l}$ in wastewater

It should be noted that the extraction coefficient value is weakly dependent on temperature and ranges from K = 1.867×10^{-4} – 2.0×10^{-4}c^{-1}. The dependence of isopropyl ether volume flow speed ϑ on the content of organic solvents and component substances in wastewater c_i can be expressed by the following equation:

$$c_i = \frac{a_0\vartheta}{1+a_1\vartheta} \qquad (4)$$

Where $\alpha_0 = 1.65, \quad \alpha_1 = 0.2$. The comparison of equation (4) and the experimental data is presented in Fig. 3.



1 – Experimental values
2 – Estimated values

Fig. 3: Comparison of estimated and experimental isopropyl consumption rate V depending on organic compound content in wastewater

A frequently encountered problem during treatment and separation of immiscible liquids with different densities is that of dispersed phase diffusion in a gravitational field. After extraction, the treated water has to be separated from the extract, which is accomplished by disengaging two immiscible liquids with different densities in settlers. Disengagement and separation of two immiscible phases are based on the physical diffusion phenomenon at the availability of an external gravitational field, since this process can be accompanied only by a diffusion effect and sedimentation or floating, depending on the medium density correlation. In order to describe extract drop behavior, one should make the following assumptions:

– All drops are strictly spherical, which is predetermined by the smallness of the Weber Number $We \ll 1$;

– Drop flow-around in the layer is viscous, which is predetermined by the smallness of the Reynolds Number $\mathrm{Re}_d = \frac{U \cdot a}{\nu_c} < 1$;

Where U is the drops speed

– Drop concentration value in the system eliminates collision and coalescence. An exception is the transfer of drops by efficient diffusion and sedimentation (floating). Taking these assumptions into account, the distribution of drops by volume i can be written for mass transfer in the form equation (5)

$$\frac{\partial c_i}{\partial t} + \frac{\partial}{\partial \lambda}\left[(U - F_i x)\right] = D_i F_i \frac{\partial^2 c}{\partial \lambda^2}$$

$$\frac{\partial P_i}{\partial t} + \frac{\partial}{\partial x}\left[(U - F_i x)\rho_i\right] = D_{\rho_i} \frac{\partial^2 \rho_i}{\partial x^2}$$

(5)

$$x = 0,\ \ c_i(x,1) = c_{10}(t) \qquad c_i(x,t) = c_{10}(x)$$

$$t = 0,\ \ \rho_i(x,t) = \rho_{10}(x);$$

$$x \to \infty,\ \ \partial c_i / \partial x \to 0$$

Where c_i is the concentration of *i*th drops, D_i is the efficient diffusion coefficient, $F_i = 1/\tau_{Ci}$ is the time constant. The general solution to the drop distribution equation (5) with boundary conditions can be written in the following form (6):

$$\rho(x,t) - \left(\frac{2KX - b}{\sqrt{2k}}\right)^m \exp\left(\frac{b}{2}\sqrt{k}\right)x - \frac{K}{2}x^2 + \frac{b}{2}\left(\frac{1}{\sqrt{2k}} - \frac{b}{Yk}\right) \times$$
$$\times \sum_{n=0}^{\infty} L_n \exp\left(\mu_n^2 D_p t\right) F\left(\frac{1}{4} + \mu_n^2; \frac{1}{4}; \frac{\xi_n^2}{4}\right) \qquad (6)$$

where $W(\xi)$ is the Whittaker function, $F_\xi(\xi)$ is the geometric function, m is a certain constant. Based on equation (6), the analytical solution is quite a complex expression, although, by using the abovementioned boundary conditions one can estimate the eigenvalues and coefficients of the L_n line. Nevertheless, in order to solve practical tasks, it is sufficient to be restricted to the first term, assuming that the line converges quickly enough. Subsequently, taking into consideration the initial condition $x = 0, \rho = \rho_0$ from equation (6) in the stationary asymptotic approximation, the following equation is obtained:

$$\rho(x) = \rho_0\left(1 - Pe\frac{x}{H}\right)\exp\left[\left(\frac{U}{2D\rho} - \sqrt{\frac{F}{2D\rho}}\right)x - \frac{F}{4D\rho}x^2\right]$$

(7)

Where $Pe = \frac{UH}{D\rho}$ is the Peclet number; H is the layer thickness.

At small flow speeds or assuming that $Pe \ll 1$, the equation can have a simpler form for drop distribution over the intermediate layer height.

4. Conclusion

The given paper suggests a new technology for treating paint-and-varnish manufacturers' wastewater with a view to removing butyl glycol, phenyl isopropanol, acetic acid and acetyl acetone by liquid-phase extraction in a stirring extractor.

An efficient extract ant was selected – isopropyl ether, which allowed extracting up to 99.8% of mass.

An efficient apparatus was selected with a view to conducting the process – a stirring extractor.

It was proven that the average drop size reduces when the breakup frequency is increased, which plays a significant role for the process implementation.

The coalescence frequency in a fluid medium was shown to depend on drop concentration, stirrer revolution speed and medium viscosity.

The model of the immiscible liquid phases' disengagement process was composed.

The paper suggests extraction treatment of the paint-and-varnish industry wastewater of organic solvents by isopropyl ether, which ensures the recirculation of recovered products and their reuse in production.

The paper provides equations for calculating the drop breakup and coalescence frequency, the interphase film, defines the experimental and estimated values of the absorbed agent concentration, reveals the dependence of isopropyl ether volume flow rate on organic solvent content.

The paper suggests conditions for dispersed system diffusion in a gravitational field.

The role of the Marangoni effect during phase coalescence, breakup and disengagement is studied.

The drop distribution over the intermediate layer height was proven to be simpler for small Peclet number values (Pe<<1).

The obtained results can be used during the design of liquid-phase extraction processes for extracting oil and oil products from wastewater of the oil-refining industry in Azerbaijan and other countries.

Conflict of interest: The authors declare that they have no conflict of interest.

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