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Removal/Reduction of Organic Pollutants from Aqueous Environment

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1. Introduction

The problem of considerable contamination of the aqueous environment with organic pollutants still requires the development of quick and simple methods for the removal, separation and determination of these compounds. The main classes of organic compounds that most of the industries use and discharge into the effluents are phenol, surfactant and dye. All these compounds are troublesome contaminants which pose not only to toxicity and health hazards but also hamper the environmental treatment processes.

In chemical industry phenol is considered as an important starting materials for numerous intermediates and finished products. It is used for the production of a wide range of consumer goods and process materials ranging from adhesives, resins, emulsifiers and detergents, plasticizers, herbicides, dyes and flavors. The worldwide production of phenol is estimated to be 5 million tons per year. Phenol and its analogues are known to be toxic to microbes. The sign of acute illness induced by phenols in experimental animals as well as in humans is known. Continuous ingestion of phenol for a prolonged period of time causes mouth sore, diarrhoea, excretion of dark urine and impaired vision at concentration levels 10÷240 ppm. Lethal blood concentration for phenol is around 1.3 g/L. phenols are toxic to several biochemical functions and to fish life. It acts as a substrate inhibitor in the bio-transformation. World Health Organization (WHO) prescribed a concentration 1 ppb as the guideline concentration in drinking water [1].

Surfactants or surface active agents are the important constituents of the synthetic detergents and may be defined as the solutes which cause the property of altering the surface or interfacial properties of their solutions to an unusual extent, even when they are present in low concentrations. Surfactants are classified according to their ionization in water, as anionic, cationic and non-ionic. The anionics are by far the most important commercially and are therefore, the once most likely to be found in streams and lakes receiving water born wastes from cities and industries. The toxicity of anionic surfactant various fishes are studied by Van Emden et al [2]. Other investigators also reported the acute and chronic effects of anionic surfactants on mice, rabbit, dog and monkey Fitzhugh et al. J.Am.Pharm. Assoc. 37,29,1948, Hopper, S, H. J. Am, Pharm. Assoc. 38, 428, 1949 [3,4]. The growth of algae as well as cause of eutrophication is reported due to the anionic surfactants. Keeping in view the various detrimental effects of anionic detergents WHO has given 0.5 ppm as its limit for general acceptibility and 1 ppm as the allowable limit of drinking water [1].

Disposal of dyeing industry waste water pose one of the major problem, because such effluents contain a number of contaminants including acid or base, dissolve solids, surfactants and color. Out of these, color is the first contaminant to be recognized because it is visible to human eye. The dye causes the harmful action to various aquatic lives. As it is resistant to light it protects the sunlight from penetrating through it and reduces the aesthetic quality of water.

Possible methods of color removal include chemical oxidation, froth flotation, coagulation, adsorption, etc. The anionic surfactants generally are removed by the chemical precipitation, foam separation, ultrafiltration and adsorption. Possible means of removal of phenols from waste water include ion exchange, reverse osmosis, chemical oxidation, precipitation, distillation, gas stripping, solvent extraction, adsorption or bio remediation.

Among the all possible technologies adsorption is found suitable for all the above classes of organics viz. dyes, surfactants and phenols. The viability of adsorption depends on the cost, stability and regeneration of the adsorbent. Removal of organic pollutants by adsorption on active carbon is used successfully for a long time [5]. But the high cost of active carbon prompted the search for other low cost adsorbents. Literature study indicates several types of adsorbent for removal of surfactants, phenols and color from waste water [6-15].

In the present communication, the fly ash, a solid waste generated from thermal power plants is chosen as the potential adsorbent for removal or reduction of pollution loads either due to 4-nitrophenol, sodium dodecyl sulphate (anionic surfactant) (SDS) or malachite green (MG). The method is simple, efficient and cost effective.

2. Materials and Methods

Compounds under observation were SDS, MG and 4-nitro phenol. All compounds were of AnalR grade from E. Mark, Germany. All the experiments were carried out in a batch mode in a shaking incubator. The batch experiments were run in different glass bottles of 100 ml capacity using average speed shaker. Prior to each experiment,1.0 g of fly ash was added to definite volume of solution taken in each bottle. The stirring was kept constant for each run through the experiments ensuring equal mixing. The desired pH was maintained using dilute NaOH/HCl solution. The bottle containing the solutions was withdrawn from the shaker at the definite time interval, centrifuged and the solute remaining in the solutions was measured spectrophotometrically (16).

3. Results and Discussion

3.1. Characterization of fly ash

In order to study the effectiveness of the fly ash as adsorbent both the physico-chemical parameters and the surface analyses are performed. The main constituents of fly ash are the SiO_2 (72.9%) and Al_2O_3 (14.5 %) with minor constituents of CaO (2.0%), MgO (0.8) and Fe_2O_3 (3.7 %). The loss of ignition is found as 8.9%. The surface area is calculated and is found to be 12.97 cm^2 and bulk density 3.24 g/cubic centimeter. The XRD (X ray diffraction pattern) and the SEM (Scanning electron microscope) photographic data at different magnifications reveal the porous texture of fly ash. Many small holes are seen on the surface of the fly ash. The high percentage of silica and alumina in fly ash together with its porous structure makes it a good candidate for utilization as an inexpensive adsorbent for bulk use.

3.2. The process optimization for attainment of equilibrium

The adsorption of organic pollutant on the fly ash surface depends on the various parameters like initial solute concentration, pH and temperature of the solutions. The dose and particle size of the adsorbent, the agitation period and agitation speed govern the attainment of equilibrium. The variables for interaction of different solutes or fly ash are indicated in the Table 1.

Table. 1. Range of operational variables during adsorption of different solutes on fly ash
Tabela 1. Zakres zmiennych operacyjnych podczas adsorpcji różnych substancji rozpuszczonych na popiele lotnym

	SDS	4-nitrophenol	Malachite green
Initial concentration (ppm)	20÷200	125÷500	75÷250
pH	2.0÷10.0	3.0÷9.0	2.0÷8.0
Temperature (K)	293÷313	293÷313	293÷313
Particle size (µm)	53÷125	53÷125	75÷500
Agitation time (min)	120	240	90
Agitation speed (rpm)	200÷400	200÷500	200÷300
Volume (ml)	20	50	50

The kinetics of solute removal at varying solute quantities at fixed FA dose follow an exponential nature. As the solute concentration increases the percent removal can be expressed as,

% adsorption = $128.0\ Co^{-0.08}$ for SDS

% adsorption = $1272.7\ Co^{-0.6477}$ for 4-nitro phenol

% adsorption = $407.4\ Co^{-0.34}$ for Malachite green

The curves are single, smooth and continuous indicating the formation of monolayer coverage on the outer interface of adsorbent [17]. Further for a fixed solute concentration as the dose of FA increases the amount of solute adsorption increases gradually. The adsorption is found to be fixed 73.0% for SDS at an initial concentration 125 ppm, 56.3% for 4-nitrophenol at an initial concentration 125 ppm and 85% for MG at an initial concentration 100 ppm. The variation of particle size greatly influenced the adsorption of all the solutes. The higher the surface area i.e. lower the particle size the more is the solute adsorption.

With increase in agitation time the solute adsorption is found to increase sharply at initial stage. The rate of increase decreases gradually as the equilibrium time is approached and becomes virtually constant near equilibrium. The equilibrium adsorption time is found to be 240 minutes for 4-nitrophenol, 120 minutes for SDS and 70 minutes for malachite green. The speed of agitation has a prominent role in determining the extent of adsorption. Higher the agitation speed the bigger is the extent of adsorption of all the studied solutes.

The temperature of the working solution plays an important role in the adsorption processes. With rise in temperature the extent of adsorption of the present solutes on FA is found to increase. This is probably due to enhanced interaction or increased equilibrium constant between solute and the adsorbent.

pH of the working solution is found to have a prominent role in adsorption. The zero point charge of the fly ash as well as the pKa of the solutes determine the pH for maximum adsorption of a particular solute. It is found that the optimum pH for maximum adsorption of SDS is 7.0, 4-nitrophenol is 6.8 and of 7.4 malachite green.

Considering all the experimental parameters the optimum conditions for the solute adsorption are presented in Table 2.

Table 2. Operational parameters for adsorption of different solutes on fly ash
Tabela 2. Operacyjne parametry dla adsorpcji różnych substancji rozpuszczonych na popiele lotnym

Operational parameters	Solutes		
	SDS	4-nitrophenol	MG
Equilibrium agitation time (min)	120	390	70
Dose of FA (gm/L)	10	20	20
PH	7.0	6.8	7.0
Particle size of FA(μm)	125	53	500

For all the solutes the agitation speed is maintained at 500 rpm and the temperature is 303K

3.3. Fly Ash-Solute adsorption isotherm

The relationship between extent of solute adsorbed on fly ash (qe) and solute concentration (Ce) at equilibrium is known as the adsorption isotherm. The interpretation of adsorption isotherm is important in the context of efficient utilization of an adsorbent and the determination of the adsorption capacity for the respective solute. The adsorption isotherm is generally expressed according to empirical relationship of Freundlich or theoritically desired Langmuir relationship. Freundlich isotherm is considered to be a special case of heterogeneous surface energies whereas Langmuir isotherm assumes the identical adsorbent surface in respect of energy. The equilibrium data for the solutes are processed in accordance with Freundlich isotherm defined by following equation:

$$qe = K \cdot C^{n}e$$

or it’s linear form

$$\log qe = \log K + n \log Ce.$$

Plot of logqe against logCe is made to yield K from the intercept and n from the slope. Fitting of the equilibrium data to the linear Freundlich equation for SDS, 4-nitrophenol and MG are made. The regression coefficient (R^2) as correlation parameter is evaluated for each individual solute. The lower R^2 value indicates that Freundlich isotherm is not applicable for the present solute – adsorbent system.

Langmuir isotherm is tested next for the present solute adsorbent system. The Langmuir isotherm is expressed as,

$$Ce/qe = 1/Q.b + Ce/Q$$

Plot of Ce/qe against Ce yields straight line with higher R^2 value (>0.98) for all the solutes studied. The Langmuir constant Q (indicative of adsorption capacity) and b (indicative of adsorption energy) are obtained from slope and intercept of the respective plot. The Langmuir model is therefore applicable in these solutes-adsorbent system.

Further, a dimensionless quantity **r**, defined as

$$\mathbf{r} = 1/1+Co\cdot b$$

is developed taking the Langmuir constant b. The parameter indicates the shape of isotherm accordingly [18].

r –value	Type of isotherm
r>1	unfavourable
r=1	linear
o<**r**<1	favourable
r=o	irreversible

3.4. Feasibility of the process

The feasibility of the adsorption of solutes on fly ash was tested from the value of free energy change (ΔG), which is related to the equilibrium constant (Kc) of the process as,

$$\Delta G= -RT\ln Kc$$

It is found that for all the solutes the free energy change is negative. The process is thus spontaneous and favorable thermodynamically. The kinetic feasibility of the process is evaluated by evaluating the t(0.5) (time for 50% adsorption) value. The shorter the t(0.5) value, the faster is the process. A comparison of the t(0.5) value for all the solutes indicates that the kinetic feasibility follows the order

MG > SDS > 4-nitro phenol in the present situation.

All the kinetic, thermodynamic and isotherm constants are furnished in Table 3.

Table 3. Kinetic, thermodynamic and isotherm constants evaluated at 303 K
Tabela 3. Stałe kinetyczne, termodynamiczne i izoterm obliczone przy 303K

Constant parameter	Solutes		
	SDS	4-nitrophenol	MG
Q(mg/g)	25.03	6.4851	9.5328
b (L/mg)	0.1979	$1.6074x10^{-2}$	0.0684
R	0.004	0.3823	0.1629
-ΔG (Kj/mole)	6.94	158.5	5.894
T(0.5) (min)	25	185	Within 10

4. Cost evaluation

Removal of SDS, 4-nitrophenol and malachite green by activated carbon is an efficient and acceptable process. But the cost of operation is very high. Therefore, the present study is undertaken using fly ash as the adsorbent. Compared to activated carbon the efficiency of removal is less in case of 4-nitrophenol and SDS. But fly ash, being a waste material, is very cheap; only the carrying cost from the site of thermal plant to the laboratory is needed. Thus the use of fly ash in removing organic pollutants appears to be a cost viable. The simplicity of the technique makes the process quite acceptable.

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Usunięcie/Redukcja zanieczyszczeń organicznych ze środowiska wodnego

Streszczenie

Obecność organicznych zanieczyszczeń w strumieniu ścieków znacznie degraduje jakość wody. Zarówno własność estetyczne jaki i organizmy wodne stają wobec niebezpieczeństwa związanego z taką degradacją. Usunięcie zanieczyszczeń organicznych szczególnie za pomącą prostych i tanich metod jest wyzwaniem dla naukowców zajmujących się środowiskiem.

Obecnie komunikaty naukowe mówią o możliwości zastosowania popiołów lotnych, odpadów stałych powstających w elektrociepłowniach, w usuwaniu albo redukcji ładunków niektórych organicznych zanieczyszczeń.

W referacie przedstawiono wyniki badań nad adsorpcją siarczanu dodecylu sodu SDS (anionowy środek powierzchniowo czynny), zieleni malachitowej MG oraz 4-nitrofenolu na popiołach lotnych. Usunięcie SDS, 4-nitrofenolu i zieleni malachitowej na węglu aktywnym jest skutecznym i zadowalającym procesem. Ale koszt tej operacji jest bardzo wysoki. Dlatego, przedsięwzięto obecne badania używając popiołów lotnych jako substancji adsorbująca. W porównaniu do węgla aktywnego efektywność usunięcia na popiołach lotnych jest mniejsza w przypadku 4-nitrofenolu i SDS. Ale popioły lotne, będąc odpadem, są bardzo tanie. W ten sposób użycie popiołów lotnych w usuwaniu organicznych zanieczyszczeń okazuje się być wykonalne pod względem kosztów. Proces jest wykonalny kinetycznie i termodynamicznie, prosty w wykonaniu i tani.