Adsorption of Detergent by Microplastics

Oz N.*, Erol Y., Yurtsever M.

Sakarya University, Environmental Engineering Department, Esentepe Campus, 54187, Sakarya, Turkey

*corresponding author:

e-mail: nuroz@sakarya.edu.tr

Abstract One of the increasing pollution loads along with the fast consuming growth in the world is microplastics which are left into the environment. 80 % of microplastic pollution in the sea moves from earth to seas. Microplastics spread toxin to water and keep hazardous contaminating chemicals on their surfaces. As a result of the ingestion of microplastics they undergo bio accumulation in the tissues and organs of organisms and they can be transfered along the food chain in the sea. In this study, detergent adsorption was investigated by using microplastic pellets in laboratory condition. To examine detergent adsorption in lab environment 0.5-2mm PP,PS and PE pellets were chosen and detergent adsorption was examined and evaluated upon pellets by preparing detergent solutions (LAS) on different conditions. As a result of these laboratory studies, it was observed that microplastics have adsorbed detergent.

Keywords: Microplastics, Adsorption, Detergents, LAS,Isoterms

1. Introduction

The plastics are synthetic polymers which are typically obtained from unrenewable sources for
example natural gas, crude oil and coal. Additionally, sea plastic crowds are one of the increasing environmental problems due to their cheap prices and wide range used (Lorena *et al*.,2010).
Especially, over the last five decades, last century almost can be described as a "plastic age" due to their existence in every part of our life. When the plastics usage get faster, microplastics amount gradually have started to grow on water resources. Most part of microplastics consist of plastics fragmentation, other part of it consist of resins shaped like small pellets which are used as industrial raw material for producing plastic products. These pellets are important carrier to support pollutions inside of the food chain, because of its durability and have ability to adsorb persistent organic pollutants (Yurtsever,2015).

It has been found that plastic deposits have direct effects on digestion in sea birds, mammals, turtles and benthic organisms, cause drowning of settled bottom creatures and accumulation of deposits of high density on the sea surface, which can prevent gas transfer between sediment and voided water (Wessel *et al*.,2016).

In this study, the adsorption of LAS, which is the raw material of detergent which is accepted as domestic waste, by microplastics such as PP, PE and PS, which are common today, has been investigated.

2. Materials and Methods

2.1. Materials

In this experiment, the adsorption of the Linear Alkyl Benzene Sulfonic Acid LAS which is leading to the most important raw materials in the detergent production process upon the micro-plastics was investigated.

Nowadays LAS is used as the main surfactant in liquids, gel or powder detergent production processes. Neutralization of LAS with Caustic Soda (sodium hydroxide,NaOH) and the addition of necessary additives (depends on usage area of produced detergent and kind of it on different concentrations) can provide the desired type of detergent (Putra *et al*.,2015).

It is the main raw material of synthetic detergent industry.Laundry, dishwasher, powder detergents, detergent gels, liquid soaps, cleaning powders, greasy soaps and etc. It issued as a mercerizing and washing agent in textile sector (Chemicalland21,2017).

The microplastics which are used to study detergent adsorption were selected as PP (Polypropylene), PS (Polystyrene) and PE (Polyethylene).

These microplastics have widespread use in nature. They are used as raw material in the sectors where food packaging, automobile supplier industry, infrastructure materials, white goods and machine parts are produced.

2.2. Experimental Procedure

The chemicals to be used were selected on the same scale based on detergent analysis method in standard methods. PP, PS and PE micro pellets widely used in nature to observe detergent adsorption were selected in 0.5-1 mm diameters.

LAS weighed as 1 g was dissolved in distilled water and 1 L was added to prepare stock solution. The solution was stored in the refrigerator to prevent biodegradation and this process was repeated weekly.

10 ml stock LAS solution was taken from the prepared stock solution; diluted 1 L with distilled water, and standard LAS solution was prepared. Phenolphthalein, 1 N

NaOH and 1N H_2SO_4 were prepared for neutralization.$CHCl_3$ and methylene blue were used to perform extraction in the separating funnels. The glass wool was used to filter out the separated solution by phase separation.After the bottom solution was filtered with glass wool,the treatments were carried out in uv-spectrophotometer to measure the adsorption values.Adsorption values were measured in uv-spectrophotometer at wavelength 652 nm. (Lepot *et al*.,2016).

3. Result and Discussion

3.1. Effects of Temperature and pH on Adsorption

The adsorption of anionic surfactant on the solid is generally proportional to the increase in temperature. When Corkill *et al*. were studying adsorption of C_8E_3 and C_8E_3 on black carbon, they examined the effect of warmth and observed that the amount of adsorption increased with increasing temperature. This experiment was run at 25 and 40 degrees and observed that the amount of adsorption at 40°C was greater. In the adsorption studies on oxyphenylene alkyl phenol has been observed that adsorption increases linearly with increasing temperature (Paria *et al*.,2004).

İt has been worked 3 different type of plastic on this study and optimum adsorption conditions were provided at pH = 3, T = 40 ° C.

The low pH and high temperature made it possible to obtain the most suitable adsorption results in the running conditions. Pinhua *et al*. mentioned the increase in adsorption rate at significant levels compared to pH = 4 and pH = 7, as a result of working with mixed surfactants (Rao *et al*,2006).

3.2.Adsorpsiton Isoterm Models

İn this work,langmuir and freundlich isoterms (Munagapati *et al*.,2017) were used to examine LAS adsorption upon microplastics..

Y.Bulut *et al*. mentioned that adsorption about langmuir isotherm increases linearly with initial adsorbate concentration.(Bulut *et al*.,2006).And they found that the surface is covered with a single layer and the amount of adsorbate adsorbed to the surface remains constant at the maximum saturation point,The linear forms of langmuir isoterm are shown in equations 1.1,1.2 and 1.3 (Hamdaouia *et al*.,2007).

$$qe = \frac{Q_{max}\, a_L\, C_e}{1+ a_L C_e} \qquad (1.1)$$

$$q_e = \frac{K_L\, C_e}{1+a_L\, C_e} \qquad (1.2)$$

If we write in a linear form;

$$\frac{1}{q_e} = (\frac{1}{K_L}).\frac{1}{C_e} + \frac{a_L}{K_L} \qquad (1.3)$$

C_e : Concentration of the remaining material in solution after adsorption (mg/L)

q_e : Amount of adsorbed material on the unit adsorbent (mg/g)

K_L : Constant dependent on the adsorption capacity of the adsorbate (L/g)

a_L : Constant dependent on adsorption energy (L/mg)

Q_{max} : Maximum Adsorption Capacity of the Adsorbent (mg/g)

The value change of $1/q_e$ relative to $1/C_e$ has been graphed after that obtained slope and cut point of the line showed us respectively the value of $1/K_L$ and a_L/K_L constants. The R^2 constant has been calculated to find the suitability of the adsorption, and this constant indicates that the availability condition is satisfied to obtain values between 0 and 1 (Aksu *et al*.,2001).

The linear forms of Freundlich isoterm has been shown in equation 1.4 and 1.5.

$$q_e = K_f C_e^{1/n} \qquad (1.4)$$

Ce: Concentration of the remaining material in solution after adsorption (mg/L)

qe: Amount of adsorbed material on the unit adsorbent (mg/g)

KF: It is calculated experimentally. Adsorption capacity (L/g)

n: Adsorption density (unitless)

In the Freundlich isotherm, the logarithm of both sides of equation 1.4 is taken and linearized. (Equation 1.5).

$$q_e = logK_f + \frac{1}{n} logC_e \qquad (1.5)$$

KF and n constants are found by plotting the value change of $logq_e$ relative to the log Ce. The cut off point of y-axis of the line obtained from the graph gives log KF and its slope gives 1/n. n> 1 indicates that the adsorption process is convenient (Acikgoz *et al*.,2016).

To find out which adsorption is better explained with which isotherm, the experimentally obtained data is applied to all isotherm equations and poured into the graph. The isotherm type of data forms a linear graph. The linear graph helps to find the correlation coefficient and is the most suitable for that adsorption.

However, the adsorption may also be suitable to one or more isoterm (Hamdaouia *et al*.,2007).

3.3. İsoterms for LAS Adsorption Upon PP

The PP adsorption was investigated at low concentrations and at different temperature and pH ranges. At the result of the studies which is completed at 3 different conditions, it was observed that the adsorption conditions suitable for PP were pH = 3, T = 40°C and langmuir isoterm have been poured by obtained data. The R^2 constant indicating suitability for adsorption indicated that the langmuir isotherm was

ropriate.(Figure1.). In order to determine the suitability of langmuir isotherm, the results were tabulated with values read on the graph.At the result of studies,it has been observed that PP has greater adsorption capacity than PE and PS under this conditions.That's why the experiments have been concentrated on PP.

(Table1.)

Table 1. Langmuir adsorption isoterm kinetics for LAS adsorption upon PP

Terms	Parameters	K_L(1/g)	a_L	R^2
pH=3 T=25°C	PP	3,22	-1,65	0,985
pH=3 T=40°C	PP	0,3	-1,01	0,9959
pH=5 T=40°C	PP	0,083	1,1	0,985

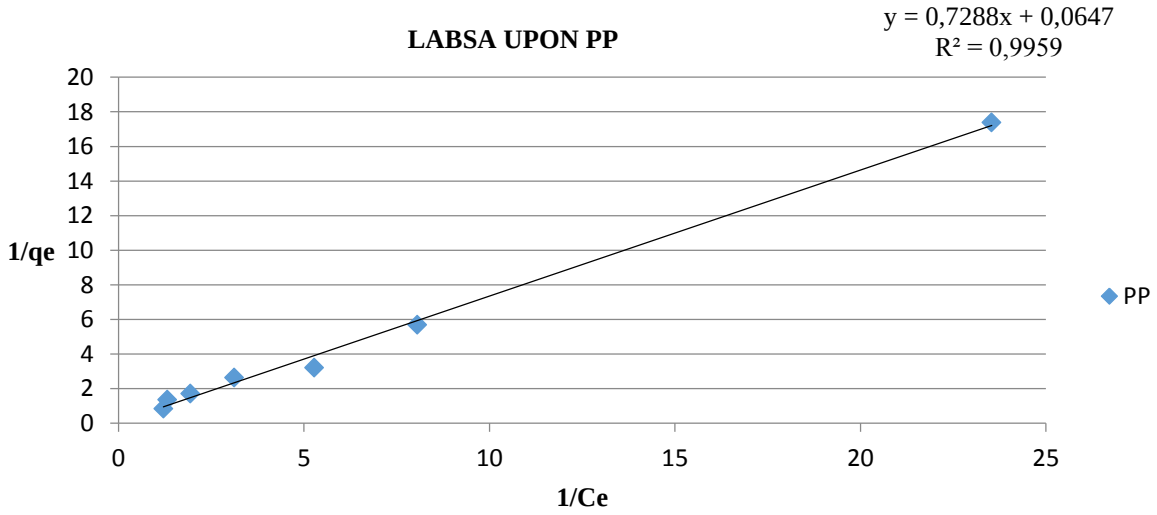

Figure 1. Langmuir adsorption isoterm for LAS upon PP on conditions pH=3,T=40°C

4. Conclusion

When considered that plastics contain hazardous additives, absorp harmful chemicals and exist freely in nature, it may be presumed that plastics will cause serious ecological problems. In this study on the deteriorated plastics that exist freely in nature, it has been observed whether detergents which are released into nature as a result of domestic and industrial processes are absorbed or not. PP, PS and PE which are found prevalently in nature, are the microplastic pellets chosen for the experiment. The studies show that the more the amount of concentration taken from detergent increases, the more absorption takes place. The amount of absorption that occurred has varied depending on the type of microplastic. It has been observed that absorption efficiency is the highest under the pH=3, T=40°C conditions. Absorption in anionic surfactants shows an increase lineally with heat. There has been a decrease in adsorption efficiency with the raise of pH. It has been detected that when pH=3, T= 40°C and pH=5, T=40°C conditions are compared, langmuir isoterm gets a more favourable coefficient of correlation under the conditions when pH is 3.

References

M.R. Lorena, R.J. Patrick, C. Moore, V.N. Urja.(2010),Quantitation of persistent organic pollutants adsorbed on plastic debris from the Northern Pacific Gyre's ''eastern garbage patch'',*Journal of Environmental Monitoring*, **12**,2189-2312.

M.Yurtsever.(2015),Microplastics:Overview,*Dokuz Eylül University Science and Engineering Journal*,**17**,63-68.

C.Wessel,G. Lockridge,D. Battiste,J.(2016),Cebrian Abundance and characteristics of microplastics in beach sediments: Insights into microplastic accumulation in northern Gulf of Mexico estuaries,*Elsevier*, **109**,178-183.

Chemicalland21,(11.03.2017),http://www.chemicalland21.com/specialtychem/perchem/LAS.htm.

M.Lepot,A.Torres,T.Hofer,N.Caradot,G.Gruber,J.B.Aubin,J.L.Bertrand.(2016),Calibration of UV/Vis spectrophotometers: A review and comparison of different methods to estimate TSS and total and dissolved COD concentrations in sewers, *WWTPs and rivers,İnternational Water Association* (IWA),**10**,519-534.

S.Paria,K.C.Hilar.(2014),A review on experimental studies of surfactant adsorption at the hydrophilic solid-water interface,*Elsevier*,**110**,75-95.

P.Rao,M.He.(2006),Adsorption of anionic and nonionic surfactant mixtures from synthetic detergents on soils,Chemosphere, **63**,1214–1221.

Y.Bulut,H.Aydın.(2006),A kinetics and thermodynamics study of methylene blue adsorption on wheat shells,*Desalination*,**194**,259-267.

O.Hamdaouia, E.Naffrechoux.(2007),Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon Part I. Two-parameter models and equations allowing determination of thermodynamic parameters,*Journal of Hazardous Materials*, **14**,381-394.

Z,Aksu,J.Yener.(2001),AComperativeAdsorption/Biosorption Study of Mono-Chlorinated Phenols onto Various Sorbents,*Waste Management*, **21**,695-702.

Y.S.Munagapati,D.Kim.(2007),Equilibrium isotherms,kinetics and thermodynamics studies for congo red adsorption using calcium alginate beads impregnated with nano-goethite,*Ecotoxicology and Environmental Safety*,***141***,226-243.M.W.A.Putra,G.Widhiantara.(2015),Adsorption of linear alklybenzene sulfanate (LAS) on eggshell powder,*Natural B.*,**3**,2.

C.Acikgöz,D.A.Sahbaz,S.Balbay.(2016),Determina-tion of Anionic Surfactant Adsorption Capacity of Expanded Perlite From Aqueous Solution,*FreseniusEnvironmental Bulletin*,**25**,3447-3453