NCNE-2020 Special Issue

J. Indian Chem. Soc.,
Vol. 97, July 2020, pp. 975-978

Use of agro-waste of *Trapa natans* plant for removal of non-ionic surfactant from industrial wastewater

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Manuscript received online 27 April 2020, accepted 01 June 2020

Demand of surfactant is rising day by day due to its multifaceted industrial applications. After use, the residual part of the surfactants gets disposed of into the water bodies without any prior treatment, which gives a toxic effect to the aquatic life. Present paper deals with the removal of nonionic surfactant octylphenol ethoxylate from industrial wastewater using agro-waste peel of *Trapa natans*. Experiments were performed through carbonized and non-carbonized peels of it. Carbonization of peel is executed in the lab in absence of oxygen at the furnace temperature 500°C. Absorbance is measured with the help of UV-Visible spectrophotometer by cobalt thiocyanate active substances procedure. A series of concentrations of surfactant solutions were prepared in the range of 200–1000 ppm. Validation of the degree of adsorption of the surfactant was done with the three adsorption isotherm models namely; Langmuir, Dubinin-Radushkevich and Harkin-Jura. Out of these three adsorption isotherms the value of regression coefficient R^2 for carbonized peel is highest for Dubinin-Radushkevich model. This is indicative of adsorption due to the formation of chemical bonds. A higher negative value of Gibb's free energy for the carbonized peel favors the maximum adsorption process. Statistical analysis of the data was dealt with ANOVA test. From the obtained results it may be concluded that the agro-waste peel of *Trapa natans* has potential to remove octylphenol ethoxylate from the industrial wastewater. The removal efficiency of carbonized peel was found better than the non-carbonized peel.

Keywords: *Trapa natans*, agro-waste, surfactant, adsorption isotherms, Langmuir, Dubinin-Radushkevich, octylphenol ethoxylate.

Introduction

Surfactants are organic chemicals, which reduce surface tension of the water or solvent[1]. Surfactants are commonly used in soaps, detergent, shampoo, cosmetic, personal care products, pharmaceutical industries and food processing industries[2,3]. It is classified into four classes anionic surfactant, cationic surfactant, non-ionic surfactant and amphoteric surfactant[4]. Toxicity of octylphenolethoxylate is reported in UK Pollution Prevention and Control (PPC) Regulations. According to it, the UK government had a voluntary agreement for the industry that octylphenolethoxylate are not to be added to domestic detergent, as it is highly lethal particularly for the aquatic organisms[5].

The broad range of surfactant application can cause side effects in the environment, so its removal takes a lot of attention to the researches. The methods available in the literature for removal of surfactants are mostly chemical methods like coagulation, flocculation with use of $FeCl_3$ and alumina[6,7], photo catalysis process[8], biological degradation method[9], absorption method for removal of cationic surfactants[10].

Generally, chemicals are used for the removal of surfactant, they transfer the problem from one phase to another phase. In the present study removal of non-ionic surfactant octylphenolethoxylate from wastewater with the help of non-carbonized and carbonized peel of *Trapa natans* is discussed. The absorption of surfactant is measured by UV- Visible spectrophotometer[11]. Removal of surfactant was calculated by Gibb's free energy, statically proven by ANOVA tests and validated by three adsorption isotherms.

Aim of the paper is to remove octylphenol ethoxylate; a non-ionic surfactant from industrial effluent and to protect aquatic life by minimizing it, in an eco-friendly and biodegradable way.

Experimental

Preparation of stock solutions:

1 *N* stock solution of ammonium thiocynate (NH_4SCN) was prepared in double distilled water and stored in airtight bottle.

Reagents: Cobalt nitrate $Co(NO_3)_2$ and benzene, used are LR grade.

Working solutions from 200 ppm to 1000 ppm concentrations of octylphenolethoxylate were prepared by the dilution method from stock solution.

Carbonization of *Trapa natas* peel [TNP] done in the laboratory using muffle furnace at temperature 500°C.

Equilibrium studies:

1 gram of each carbonized and non-carbonized agro char were taken in an airtight bottle. Shaken it for adsorption process with different concentrations of 200 ppm to 1000 ppm of 50 ml surfactants solution up to 35 min. The mixture is allowed standing for 15 min. After filtration filtrate was treated with 20 ml of 1 *N* ammonium thiocyanate solution with 0.3 ml of cobalt nitrate. The solution was poured into separating funnel and allowed to stand for 15 min to settle down[12]. After the formation of two separate layers, analysis is processed for absorption in UV-Visible spectrophotometer.

The statistical analysis ANOVA was performed on the absorbance of surfactant by the peel of non-carbonized *Trapa natans* and carbonized *Trapa natans*. This is calculated by computer software SPSS.

Adsorption isotherms:

Absorbance of surfactant octylphenolethoxylate by per one gram non carbonized and carbonized agro waste is calculated by the equation:

$$x = Ce.V.Eq/1000 \qquad (1)$$

where x = number of moles of surfactant, V = volume of the solution in ml, Eq = equivalent weight of surfactant in gram.

Adsorption process can be represented by adsorption isotherms. It is the graph which shows the amounts of adsorbate, adsorbed on the surface of adsorbent at a constant temperature.

Langmuir adsorption isotherm:

Monolayer adsorption on the adsorbent bed is applied in this isotherm[13]. This is calculate by following equation,

$$\frac{1}{q} = \frac{1}{Q_o} + \frac{1}{Q_o K_L C_e} \qquad (2)$$

where C_e = concentration of adsorbate, q = quantity of the substance adsorbed, Q_o = capacity of the single-layer absorption.

Dubinin-Radushkevich adsorption isotherm:

Adsorption on the homogeneous and heterogeneous surfaces can be explained by this model. The non-linear equation can be shown as:

$$q = qs \exp(-K_{DR}\,\varepsilon^2) \qquad (3)$$

ε is denoted for the Polanyi potential. This model is useful to found out the mean free energy of adsorption E. Value of E predicts the statements – If $E < 8$, denotes the physical adsorption process and $E > 8$ processes will be chemical adsorption among adsorbate, adsorbed and adsorbent materials[14].

Harkin-Jura adsorption isotherm:

This model showed the potential of the heterogeneous system to adsorb material, in manifold layers on the surface of adsorbent[15]. Liner equation express as:

$$\frac{1}{q^2} = \frac{B}{A} - \frac{1}{A}(\log C_e) \qquad (4)$$

where, A and B are Harkin-Jura constant.

Thermodynamic parameters:

Gibb's free energy: High negative value of ΔG is indicating the possibility of the reaction[16]. This is calculated by equation,

$$\Delta G = -RT \log K_L \qquad (5)$$

where ΔG = change of free energy, R = gas constant, T = the absolute temperature in Kelvin.

Results and discussion

The molecular formula of octylphenolethoxylate is $C_{14}H_{22}O(C_2H_4O)_n$ (n = 9-10). It is a non-ionic surfactant. The structural formula of octylphenol ethoxylate is shown in Fig. 1.

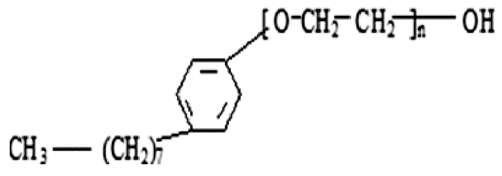

Fig. 1. Structural formula of octylphenol ethoxylate.

Mechanism for reaction:

On addition of cobalt nitrate and ammonium thiocyanate pink colour complex is obtained. This pink complex is added in non-ionic surfactant to form a blue colour complex dye.

$$CoNO_3 + 4NH_4CNS \rightarrow (NH_4)_2[Co(CNS)_4] + 2NH_4NO_3 \quad (6)$$

$$(NH_4)_2[Co(CNS)_4] + \text{Non-ionic surfactant} \rightarrow \text{Blue coloured complex dye}^{11} \quad (7)$$

Coloured complex is measured by UV spectrophotometer at λ_{max} of 467 nm. The statistical analysis ANOVA performed on the absorbance of surfactant by adsorption bed on non-carbonized and carbonized agro-waste the variance of ANOVA were calculated significant value at p = 0.044 and 0.009 respectively..

Study of adsorption isotherms model:

According to the present study, all data given in Table 1.

Langmuir adsorption isotherm:

The numeric values of q and K_L were obtained from the slope and an intercept from Langmuir graph of $1/q$ versus $1/C_e$. The focal point of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L[17]:

$$K_L = 1/1 + (1 + K_L\, C_i) \quad (8)$$

If R_L>1 non-favorable, if R_L = 1 linear relation and if 0< R_L < 1 favourable. In the present study the data interpreted in Table 1, the value of R_L is more than 0 but lesser than 1 it supports Langmuir isotherm is shown in Fig. 2.

Dubinin-Radushkevich isotherm:

According to this isotherm linear graph plot by eq. (3), as shown in Fig. 3. In the present study, the E value for non-carbonized and carbonized *Trapa natans* peel are 11.22 kJ mol^{-1} and 11.41 kJ mol^{-1} respectively. This reflects the chemical bond forms between surfactant and adsorbent.

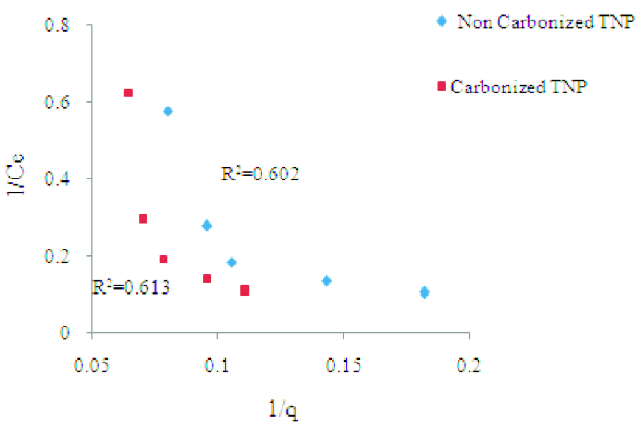

Fig. 2. Langumuir adsorption isotherm.

Table 1. Adsorption isotherm parameters and Gibb's free energy of surfactant after absorption by non-carbonized and carbonized peel of *Trapa natans* agro-waste

Adsorption isotherm	Parameter	Unit	Peel of non-carbonized *Trapa natans*	Peel of carbonized *Trapa natans*
Langmuir	Q_{max}	mg g^{-1}	0.0637	0.0309
	K_L	L mg^{-1}	1.64	3.539
	R_L		3.030×10^{-3}	1.414×10^{-3}
	R^2		0.602	0.613
Dubinin-Radushkevich	q_{DR}	mg g^{-1}	2609.85	1376.91
	β	mol^2 kJ^{-1}	3.975×10^{-3}	3.837×10^{-3}
	E	kJ mol^{-1}	11.223	11.415
	R^2		0.733	0.928
Harkin-Jura	A	mol g^{-1}	4.631	4.899
	B	mol g^{-1}	0.011	0.037
	R^2		0.729	0.751
Gibb's free energy	ΔG	kJ mol^{-1}	–5.39	–13.827

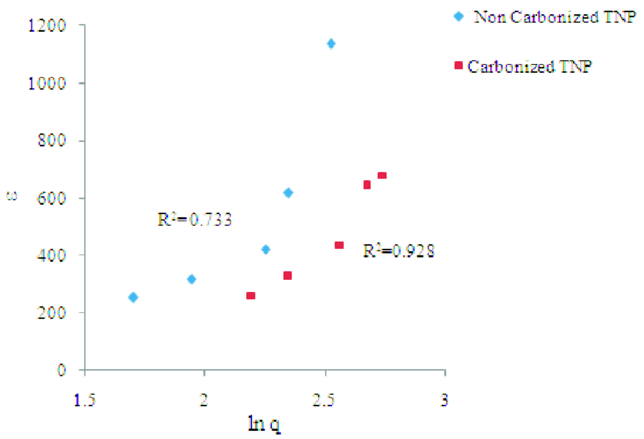

Fig. 3. Dubinin-Radushkevich adsorption isotherm.

Harkin-Jura isotherm:

In this adsorption isotherm R^2 value for non-carbonized and carbonized agro-waste with a surfactant is 0.823 and 0.923 respectively as shown in Fig. 4. R^2 value gives a supportive statement that multilayer adsorption take place on the surface of adsorbent in the heterogeneous system.

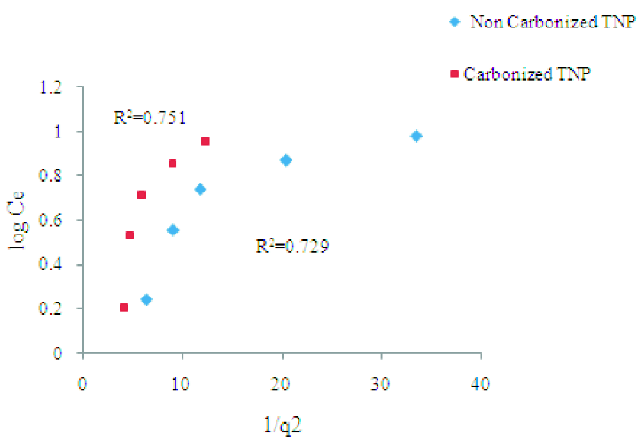

Fig. 4. Harkin-Jura adsorption isotherm.

Gibb's free energy:

Under the thermodynamic parameters considers Gibb's free energy. A high negative value of ΔG has shown the feasibility of the reaction. Both adsorbent beds give negative value this indicates maximum absorbance takes place.

Conclusions

In this paper elimination of surface-active agent octylphenol ethoxylate from industrial effluent was done by non-carbonized and carbonized peels of *Trapa natans* agro-waste. Absorbance was taken by UV-Visible spectrophotometer at λ_{max} of 467 nm. Three adsorption isothermic models Langmuir, Dubinin-Radushkevich and Harkin-Jura were studied. Results listed in Table 1 indicates that the value of regression coefficient R^2 for Dubinin-Radushkevich adsorption isotherm is higher than other isotherms, it supports the formation of chemical bonds between them so adsorption of surfactant is in the maximum amount. The trend of adsorption is same for both heterogeneous and homogeneous system. The variance of ANOVA at p = 0.009 is also in favour of the adsorption process. The high negative value of Gibb's free energy confirms that carbonized *Trapa natans* peel may have sufficient potential to be an active bio-adsorbent for the elimination of octylphenolethoxylate from industrial effluent. As per reaction mechanism on addition of cobalt nitrate and ammonium thiocyanate pink coloured complex is obtained. This pink complex is added in non-ionic surfactant to form a blue coloured complex dye.

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