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Research Paper

Investigating the Isotherm, Kinetics, and Thermodynamics of the Adsorption of Pollutants from the Wastewater of Sari Oil Refinery by a Pilot Rotating Disk Reactor Covered with Graphene

Maryam Sadat Mirneamati*

Faculty of Environment, Oil Pipelines Company, Sari, Mazandaran, Iran

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1. ABSTRACT

In this research, the application of adsorption isotherm, kinetic and thermodynamic models in a rotating disk reactor covered with graphene nanoparticles designed to remove aromatic compounds from the wastewater of the refinery located in Sari oil facilities and as a result reducing the chemical oxygen demand (COD) of the wastewater was investigated. Langmuir-Freundlich thermocouple was used to investigate the removal process. Also, the adsorption kinetics were investigated by pseudo-first-order, pseudo-second-order and interparticle diffusion models. The thermodynamics of adsorption was studied by Vant Hoff relation and its results were analyzed. Also, the effect of the effluent concentration parameters (70, 100, 150 mg/L COD) and temperature (20, 30, and 40 °C and effluent retention time) on the effluent COD removal rate was investigated. The results showed that the rate of COD absorption and reduction of wastewater increased with the increase of wastewater concentration and process temperature, and under optimal conditions, it was equal to 66%. The applicability of two isothermal equations in the form of Freundlich-Langmuir and kinetic models were determined as pseudo-second order > interparticle diffusion > pseudo-first order. Also, the parameters of the thermodynamic equation changes in free energy (ΔG), changes in enthalpy (ΔH) and entropy (ΔS) showed that the absorption process was spontaneous and the irregularities in the system increase. The percentages the reduction of effluent COD for concentrations of 70, 100 and 150 mg/L was equal to 48%, 62% and 73%, respectively. At 40°C, the percentage of COD reduction is about 70%, which is the highest percentage obtained at different test temperatures. The percentage of removal for temperatures of 20 and 30 was not different from each other. It was 65.2% and 67.6%, respectively.

Keywords: Aromatic Compounds, Graphene, Surface Adsorption, Isothermal, Adsorption Kinetics, Adsorption Thermodynamics.

2. INTRODUCTION

Wastewaters from oil pipeline treatment plants have a wide variety of cyclic hydrocarbons, organic solvents, aromatic compounds, aldehydes, and many other substances. According to RCRA classification 1, the materials obtained from oil refining are included in the list of hazardous waste materials. Several technologies have been proposed to reduce the amount of aromatics in wastewater, such as the use of sequential anaerobic-aerobic treatment series and the use of electrochemical processes, all of which are time-consuming and expensive. It seems that using the adsorption process can be a simpler process that is well combined with biological purification. Their diverse structure and high active level have been able to gain their place as very suitable adsorbents among researchers [1-4]. In this research, for the first time, a rotating disc reactor covered with graphene nanosheets was designed and used to complete the anaerobic biological treatment of the actual effluent of Sari oil facilities. The obtained laboratory data were analyzed in order to investigate adsorption isotherms, adsorption kinetic-thermodynamic models of graphene nanoparticles in the reactor.

3. MATERIALS AND METHODS

Graphene used in this research was purchased from ACS Materials, USA with BET surface area of 650 m^2/g. and DMF solvent are from MERCK, Germany. The wastewater used in the research was prepared and used from the Sari oil facility and from the second anaerobic treatment outlet of the treatment plant. The reactor designed in this research has a plexiglass

* mirnemati.m.1993@gmail.com

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body with a height of 50 cm and an internal diameter of 9 cm, a useful volume of 3.9 L and an operational volume of 2 L. The stainless steel rod was considered as its axis, on which three metal discs with a diameter of 6 cm, which can be separated from the axis, were placed.

3.1. Adsorption tests

0.01 g of graphene was dissolved in 10 mL of solvent and then mixed well for 30 minutes and then subjected to ultrasound for 15 minutes. All the obtained solutions were used for coating 4 mica sheets. Due to the brittleness of the mica plates, stainless steel discs were used as holders for these plates inside the reactor, and the mica plates were connected to the metal discs using aquarium glue. In order to investigate the effect of different concentrations on the percentage of aromatic substances removal and COD reduction, the amount of chemical oxygen-demand (mg/L) was used as different concentrations. And for three concentrations of COD (70,100,150 mg/L) experiments were carried out. The pH =7 and temperature 40°C was considered constant. Temperatures of (20, 30 and 40˚C) were chosen to test the effect of paratherm on aromatics absorption and COD reduction. pH=7 and the concentration of COD: 150 mg/L was considered constant. In order to investigate the effect of pH on the percentage of aromatics removal and COD reduction, experiments were conducted at different pH levels of 5, 7, and 9, at a constant temperature of 40°C, and at a constant concentration of 150 mg/L COD. According to the effluent analysis, the pH of the second anaerobic output was equal to7.1, and H2SO4 and NaOH were used to make it acidic and alkaline, respectively. An automatic pH meter (pH Meter BASIC 20+ Crison, EU) was used to check pH.

4. RESULTS AND DISCUSSION

4.1. Check operational parameters

One of the reasons that affects the rate of absorption in high concentrations of wastewater is the concentration gradient that is created in the wastewater from liquid to solid phase (adsorbent). At high concentrations, this concentration gradient is very high. And for this reason, the speed of absorption is high, but with the reduction of the concentration, the strength of the concentration gradient is reduced and the speed of absorption decreases [5]. The COD reduction percentages for concentrations of 70, 100, and 150 mg/L were 48%, 62%, and 73%, respectively. At 40°C, the percentage of COD reduction is about 70%, which is the highest percentage obtained at different test temperatures. The percentage of removal for temperatures of 20 and 30 does not differ much from each other and is equal to 65.2% and 67.6%, respectively. At high temperature, the mobility of pollutants in the wastewater is higher, and for this reason, the possibility of them hitting the graphene surface and being absorbed on it is high. It is possible that due to the increase in temperature, the graphene will be swollen and the layers will be separated. This swelling causes space and consequently more surface area to be created for absorption within the internal structure of the absorbent, which causes Large molecules penetrate more into graphene and get absorbed in it. This process is called intermediation, which is one of the factors that affects the absorption and increases the yield.

4.2. Investigation of absorption isotherms

The R^2 correlation coefficient for the Langmuir isotherm shows the best possible value and a very favorable linear relationship for absorption can be seen. A very high correlation coefficient was also observed in the Freundlich isotherm model In the Freundlich isothermal model, the value of n indicates the optimal absorption. n between 2 and 10 indicates optimal absorption and n between 1 and 2 indicates normal absorption. For n smaller than 1, the absorption is relatively difficult. As it is known, this value was greater than 1 for the absorption process, which indicates normal and relative absorption on graphene. As it is clear from the numbers, tables and diagrams, the absorption follows the Freundlich and Langmuir isotherms and the absorption is relatively normal, and this normal absorption is due to the fact that the absorption process by graphene is due to the need to swell the graphene layers and the possibility of the penetration of aromatic molecules. Into the layers is a slow process that we that we expected to have a good absorption.

4.3. Examination of absorption kinetics

The highest correlation coefficients are related to the second-order pseudo-equation and the lowest are related to the first-order pseudo-equation. The values of the calculated variables of these equations are given in Table 1.

concentration	Quasi first degree			Quasi second degree			Intermolecular penetration		
	q_e (mg/g)	K^2 (min)	R^2	q_e (mg/g)	K^2 (g/mg .min)	R^2	C	K_{id} mg/g $min^{1/2}$	R^2
150	950	0.1	0.966	2500	1.2	0.999	2.01	0.07	0.974
100	958	0.62	0.961	833	1.1	0.998	0.34	0.05	0.827
70	955	2	0.932	178	3.2	0.987	0.03	0.02	0.787

4.4. Investigation of thermodynamics of absorption

The negative value of ΔG for different temperatures indicates that the absorption in the system is spontaneous. The positive values obtained for the variable ΔS indicate the irregularity of absorption in the solid/solution surface of the system during the absorption process. This may be due to the increase in swelling of graphene with increasing temperature, which favors absorption.

By calculating the enthalpy change variable (ΔH) from the chart, a positive number was obtained. It can be said that due to the surface adsorption of aromatic molecules on the graphene surface and the establishment of π-π interactions, the energy level of the aromatics and as a result the energy level of the system is found and causes the release of heat. This amount of energy is not enough for the graphene corona layer to swell, and the heating is done and the absorption is better [4].

5. CONCLUSION

It was determined that increasing the concentration and efficiency of the adsorbent has a positive effect, and the removal of COD improves. It has been absorbed and at high temperatures it has this effect of increasing molecular movement and swelling of graphene layers. The R^2 correlation coefficient for the Langmuir isotherm shows the best possible value and a very favorable linear relationship for absorption can be seen, and also the values of n in the Freundlich isotherm are greater than 1, which indicates normal and relative absorption. It is graphene. In the absorption kinetics section, the highest correlation coefficients related to the pseudo-second order equation and the lowest correlation coefficients related to the pseudo-first order equation were obtained. The second-order quasi-kinetic model had the highest correlation coefficient, followed by the interparticle penetration model, which, according to the obtained values, shows that the main adsorption mechanism was surface adsorption and the boundary layer effect. It is a little bit. From the calculation of thermodynamics of adsorption, negative ΔG values were obtained, which drives the spontaneity and irregularity of the adsorption mechanism. A positive ΔS indicates that graphene needs to be inflated for better absorption.

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