Int. J. of Thermal & Environmental Engineering
Volume 15, No. 1(2017) 57-61

Reducing Organic Pollution of Wastewater from Milk Processing Industry by Adsorption on Marlstone Particles

Maher Al-Jabari*, Hiba Dwiek, Nareman Zahdeh, Nadia Eqefan

Environmental Technology Engineering, Palestine Polytechnic University, Hebron, Palestine

Abstract

This paper presents a simple technique for controlling industrial pollution of wastewater with organic content. It summarizes results of an experimental batch adsorption work. Samples of real wastewater from milk processing are mixed with marlstone particles and the COD is measured as a function of time for monitoring the performance and kinetics of the adsorption process. Kinetic curves of COD in wastewater and surface concentration (on marlstone particles) as well as equilibrium data are presented. Effects of various parameters are investigated and including stirring rate, pH, solid to liquid ratio (dosage), organic load and contact time. The equilibrium adsorption isotherm is obtained and found to be unfavorable type. Equilibrium adsorption capacity is pH dependent, as adsorption process favors moderate alkaline conditions, i.e. pH range of 5-9. Removal efficiency increases with increasing marlstone particles to wastewater ratio. The adsorption process is relatively fast upon stirring the system as the rate of adsorption increases with stirring rate. Under stirring the final equilibrium adsorption is reached within four hours while without stirring, the adsorption process takes more than 10 days to reach to an equilibrium state. The obtained experimental kinetic adsorption curves are modeled using pseudo first order and second order rate equations.

Keywords: *wastewater, chemical oxygen demand, adsorption, kinetic, equilibrium, marlstone*

1. Introduction

Most of industrial wastewater in Palestine is discharged directly into sewer system (62.8 %). The rest (37.2 %) is discharged through cesspits [1]. For dairy effluents, biological oxygen demand (BOD) and chemical oxygen demand (COD) average values were 1941 ± 864 ppm, 3383 ± 1345 ppm, respectively [2]. Dairy wastewater was found to have a pH of 7.9 ± 1.2 and TSS of 831 ± 392 [2]. For the last decades, there have been limited efforts for controlling wastewater from dairy industry in Palestine.

Various treatment methods are used for wastewater effluent from dairy industry. These include activated sludge, trickling filters, up flow anaerobic sludge blanket, nano filtration and others. These techniques are complicated, expensive, energy consuming and unable to reduce and meet the effluent discharge standards of 50 ppm BOD and 250 ppm COD according to World Bank restrictions [2].

Adsorption is one of these treatment methods. Organic material in dairy wastewater can be adsorbed onto various solid adsorbents. Previous studies and researches have confirmed the technical feasibility of adsorbing organics on various adsorbents. These adsorbents include low molecular weight crab shell chitosan [3], activated carbon commercial grade (ACC) [4], bagasse fly ash (BFA) [4], acid mine drainage sludge [5], and Neem leaves powder [6]. Investigated parameters in these studies included; pH, particle dosage, contact time, stirring rate and initial concentration of organics. In previous publications, the technical feasibility of utilizing marlstone in reducing chromium concentration in tannery wastewater was confirmed and investigated experimentally [7, 8].

In most of the previous adsorption studies, empirical models were used to fit experimental kinetic curves (e.g. Elovich and Lagergren pseudo-first order and second-order models). Adsorption models (second-order) were reviewed by Ho [9]. First order model was used by Elagroudy to estimate the mass adsorbed in i^{th} minutes (M_i) [10].A full review of modeling papers is available in the literature [11]. Two theoretical models

* Corresponding author. Mobile: 0599723669
E-mail: mjabari@ppu.edu

DOI: 10.5383/ijtee.15.01.007

for adsorption kinetics were published recently; one was based on mass transfer [12] and the other one on Langmuir kinetics [13].

Adsorption is the simplest solution for reducing COD in dairy industry wastewater. When a low cost abundant adsorbent is used, adsorption is most preferred. A previous paper by the authors had demonstrated the technical feasibility of treating dairy wastewater with various local abundant adsorbents [14]. The same local adsorbents were also used to treat other types of industrial waste water such as leather tanning wastewater [7, 15]. Recently, the authors of this paper published a paper dealing with the adsorption of pollutants from dairy wastewater on soil particles [16]. No previous work handled the marlstone particles for adsorbing organic pollutants.

In this work, an experimental study is reported on using marlstone as an adsorbing solid. The effects of various operating parameters on batch adsorption process were investigated. These parameters including solid content, pH, stirring rate, contact time and organics initial concentration. The obtained experimental kinetics was fitted to empirical kinetic models.

2. Material and Methods

Samples of several grams of marlstone were obtained from local areas (Hebron, Palestine). Samples were dried in an oven at 120 ^{o}C for several hours. The size of marlstone particles was determined to 53 µm, using sedimentation method.

Real samples of dairy wastewater were obtained from a local dairy factory (AL-Jebreni Company, Hebron, Palestine). Wastewater samples are stored in a refrigerator at 4 ^{o}C. An amount of 2 mL of concentrated sulfuric acid (18M, 99% purity) is added to each liter of wastewater to prevent natural biodegradation [17]. It is diluted at a ratio of 1:10 using distilled water. Chemical reagents used include Potassium Dichromate, Sulfuric Acid 99% purity, Potassium Hydrogen Phthalate, 1.1 Phanthroline and Ferrous Sulfate. All chemicals are obtained from Sigma Aldrich.

For batch adsorption experiments, a volume of 100 mL of wastewater is mixed with a certain mass of marlstone particles. All adsorption experiments were performed at ambient room temperature (22^{o}C) in stirred vessels using mechanical shaker. At certain time intervals, small samples of wastewater are then taken from the adsorption vessel and analyzed using standard COD test procedure [17].

The efficiency of the adsorption process is obtained from the percentage COD reduction, as given by the following equation:

$$\text{Percentage removal of } COD = \frac{COD_o - COD_t}{COD_o} \times 100\% \qquad (1)$$

Where COD_o is the initial COD of wastewater (mg/L), COD_t is the obtained COD at certain time (mg/L).

The adsorption capacity, q_t, in mg/g is obtained by the batch mass balance for adsorption process as follows:

$$q_t = \frac{V(COD_o - COD_t)}{m} \qquad (2)$$

Where m is the mass of adsorbent in grams and v is the volume of wastewater for each batch of 100 mL.

The validity of monitoring COD reduction in dairy wastewater for evaluating performance of wastewater treatment processes has been previously demonstrated [2,18]. The removal of organic pollutants from dairy wastewater using marlstone particles was compared with that utilizing limestone and soil particles. Equilibrium was approached for all types of adsorbents within a period of less than 5 hours, when the system is stirred. For a dosage of 5% solids (by weight), the removal efficiency was found to be close for marlstone and soil particles (26% and 23% respectively), while it jumped up to 68% for non-flocculated stone cutting particles.

Figure 1 demonstrates the adsorption kinetic curve (as a plot of COD versus time). It shows two groups of experimental data obtained from two identical adsorption experiments (circles and squares), with a particle dosage of 5 g/100 mL, and at a temperature of 22 ^{o}C, pH= 6 and stirring rate of 250 rpm. It clearly confirms the reproducibility of data and the validity of experimental procedures. The organic load in wastewater decreases with time as a result of its adsorption onto the surface of marlstone particles as shown in Figure 1. Simultaneously, the equivalent surface concentration (q_t) increases with time (the red curve in the secondary ordinate of Figure 1); since mass balance enforces that what is lost from solution is gained by the surface. At equilibrium, the rate of adsorption equals the rate of desorption, and thus no further net change in COD occurs, resulting in constant equilibrium value. Figure 1 indicates that the adsorption process is relatively fast and the equilibrium is achieved within 3 hours.

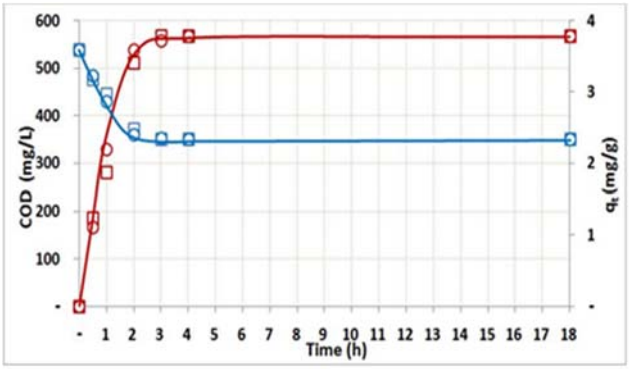

Fig. 1. Reproducible kinetic curve of adsorption capacity of marlstone particles with a dose of 5 g/100 mL at 22oC, stirring rate= 250 rpm and pH=6 (squares for trial 1 and circles for trial 2).

3. Results and Discussion

3.1. Effect of marlstone particles dosage

Increasing the particle dosages has major effect on final removal efficiency as it increases the total available surface area for adsorption. Figure 2 shows the adsorption kinetic curves for three cases of marlstone particle dosages of 1, 5, and 10 g/mL. All experiments are performed at pH=6, a temperature of 22 ^{o}C and a stirring rate of 250 rpm. At high particle dosage of 10 g/100 mL, the obtained $q_t$is2.5 mg/g and the removal efficiency is 45.7%. Figure 2 also shows that changing particle dosage affects the adsorption rate. Increasing the particle dosage increases adsorption rate. It decreases the time needed to approach equilibrium by increasing the slope of the kinetic curve at a given time. This attributed to the fact that with more particles in liquid, more collisions occurs with their surfaces and leading to faster adsorption.

3.2. Effect of pH

It is well known that adsorption on surfaces is pH dependent. Figure 3 shows the obtained results of equilibrium removal efficiency as a function of solution pH using a particle dosage of 5 g/100 mL at a temperature of 22 ºC and stirring rate of 70 rpm. A wastewater pH range between 2 to 12 is obtained by adjusting pH using concentrated hydrochloric acid and sodium hydroxide. Samples using the same mass (5 g/100 mL) with different pH values were stirred for 18 hours and allowed to settle for 24 hours to obtain the final equilibrium value of COD. Obviously, lower COD percentage reduction is observed at extremely acidic and alkaline solutions. There is a limited pH range for adsorption, which is nearly 5-9, with maximum removal efficiency of 32% at pH=6.

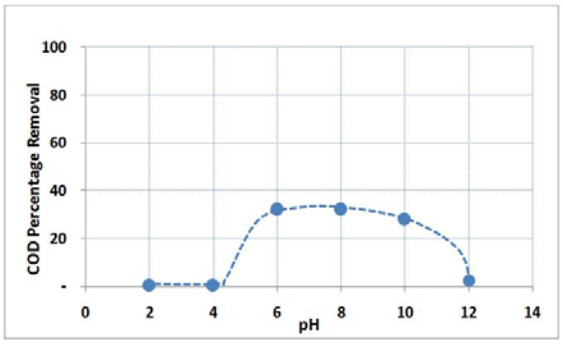

Fig.3. COD percentage reduction as a function of pH using a dose 5 g marl/100mL at 22 ºC and 70 rpm.

3. 3. Effect of stirring rate

The above fast adsorption rate is obtained under system stirring, that keeps particles suspended in the vessel. When adsorption vessel is left unstirred the particles are settled at the bottom of the vessel leading to an extremely slow adsorption process. Figure 5 shows results obtained for adsorption experiment at the similar conditions of those reported in Figure 1 but without stirring. Approximate 10 days were required to reach nearly the same equilibrium COD value as to those reported for the stirring case in Figure 4. This is attributed to the fact that the adsorption process is mass transfer driven. It is believed that the liquid side mass transfer resistance controls the process. Thus, the adsorption rate increases with bulk motion. The effect of increasing stirring rate is presented in Figure 4 (for similar conditions as in cases in Figure 1 and Figure 5).

At low stirring speed of 70 rpm, equilibrium is approached within about 4 hours, which is larger than the time period for the case with 250 rpm (about 2 hours). The final removal efficiency does not change with bulk motion, since it is characterized by the equilibrium adsorption capacity. Adsorption capacity is a surface property and does not depend on the surrounding hydrodynamic conditions.

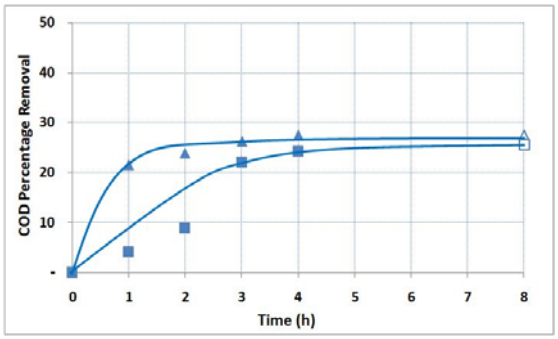

Fig.4. Percentage COD reduction as function of time at two stirring rates (squares for 70 rpm and triangles for 250 rpm) at pH=6, 22 ºC and a dose of 5 g marl/100 mL.

3.4. Effects of organics initial concentration

After sufficient times, the kinetic curves levels off, then, the obtained COD_e and equivalent q_e values represent equilibrium concentrations. They are plotted to obtain equilibrium isotherm. Figure 6 the obtained isotherm for adsorption on marlstone particles. This isotherm is concaved up, and thus it is of unfavorable type. This type of dependence is of great importance as natural adsorption of organics is not easy.

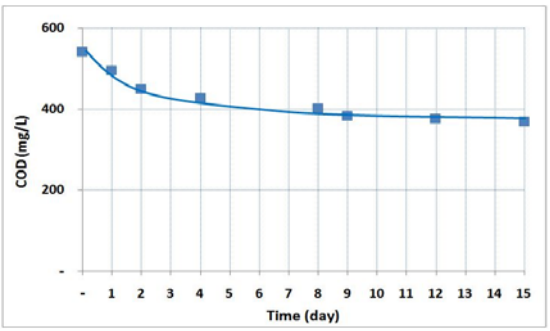

Fig.5. Adsorption kinetics (COD versus time) for adsorption on stagnant particles (no stirring) using 5 g marl/100 mL at 22 ºC and pH=6.

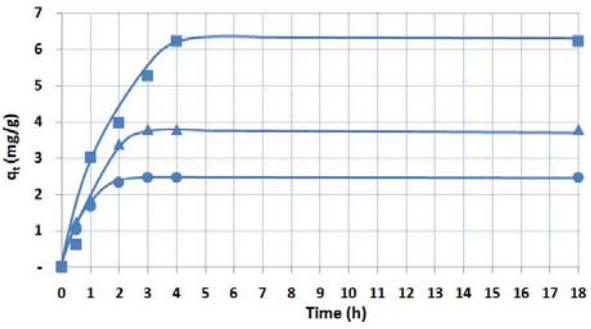

Fig.2. Effect of marlstone dosage on the kinetic adsorption curves (qt) (circles for 1 g/100mL, triangles for 5 g/100 mL and squares for 10 g/100mL) at pH=6, 22 ºC and stirring rate= 250 rpm.

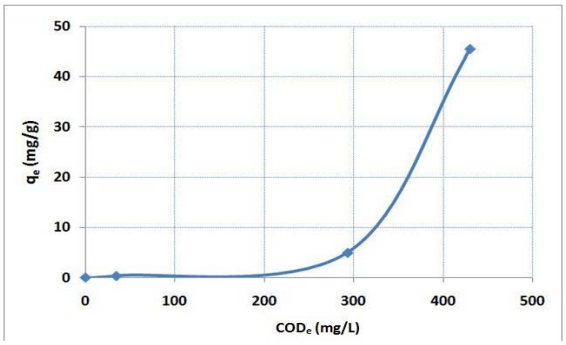

Fig.6. Adsorption isotherm for a dose of 10 g/100 mL at 22 ºC and pH=6.

3.5. Modeling adsorption kinetics

The previous mathematical models [12, 13] are not suitable for this adsorption kinetics; since the equilibrium adsorption is not linear, or Langmuir type. A future work is suggested to update the existing mass transfer model with Frendlich equilibrium isotherm. However, the obtained experimental kinetic adsorption curves are modeled using pseudo first order and second order rate equations, given in equation (3) and equation (4) [together with equation (5)], presented in linear forms[19].

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{V_o} + \frac{1}{q_e} t \quad (4)$$

$$V_o = K_2 {q_e}^2 \quad (5)$$

Where K_1, K_2 in (h^{-1}) are the pseudo first order and second order rate constants for the kinetic models respectively. q_e and q_t in (mg/g) are the adsorption capacities at equilibrium and at a time t in (h), respectively, and V_o in (mg/g·h) is the initial adsorption rate.

With the first order model, the plot of log (q_e– q_t) versus time is linear, with a negative slope of (–K_1/2.303). The obtained modeling results are plotted in Figure 7, using this first order model, and the obtained model and fitting parameters are listed in Table 1.

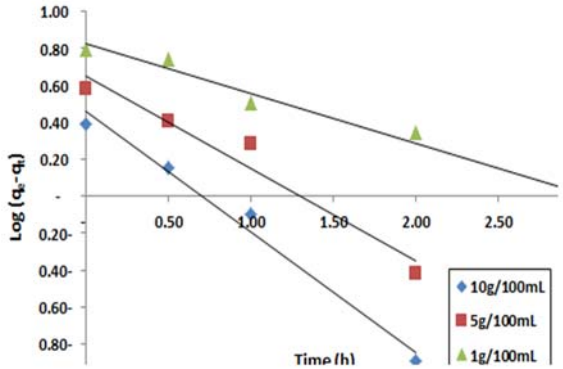

Fig. 7. First order kinetic model for the adsorption of organic molecules onto marlstone particles for different dosages.

Table 1. Obtained model and fitting parameters with pseudo first order model for the adsorption of organic molecules onto marlstone particles.

Dose (g/100mL)	q_e (mg/g)	K_1 (h^{-1})	R^2
1	6.70	0.623	0.9724
5	4.46	1.154	0.9528
10	2.86	1.496	0.9826

With the second order model, the plot of t/q_t versus time is linear, with a positive slope of $1/q_e$. The resulting lines for the second order model are plotted in Figure 8, and the obtained model and fitting parameters are listed in Table 2. Obviously, the pseudo second order model gives better fitting than the first order model (i.e., higher R^2values).

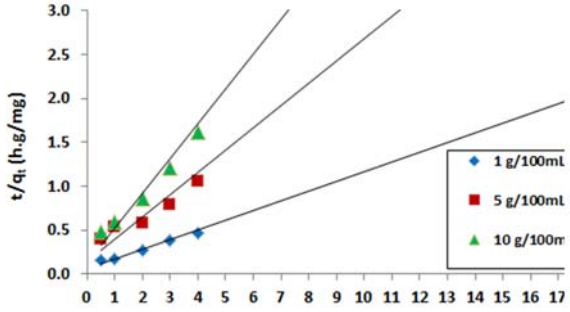

Fig.8. Second order kinetic model for the adsorption of organic molecules onto marlstone particles for different dosages.

Table 2. Obtained model and fitting parameters with pseudo second order model for the adsorption of organic molecules onto marlstone particles.

Dose (g/100mL)	V_o (mg/g.h)	q_e (mg/g)	K_2 (h^{-1})	R^2
1	15.38	9.090	0.1861	0.9988
5	6.670	3.950	0.4275	0.9954
10	7.668	2.528	1.1998	0.9984

.

4. Conclusion

This paper demonstrates that marlstone can reduce the organic load (COD) in dairy industry wastewater. The percentage reduction of COD increased with increasing contact time until equilibrium is achieved and the reduction is directly proportional with the solid content. 45.7% reduction in COD was obtained using 10 g/100 mL of the adsorbent. The optimum pH in the current experiments was in range of5-9. Increasing the stirring rate minimized the needed time to level off without affecting the COD percentage reduction. The non-stirred experiments (static) required more time to treat and remediate dairy wastewater. The pseudo second order empirical model provides better fitting than the first order model.

Nomenclature

COD	Chemical oxygen demand, mg/L
COD_O	Initial COD of wastewater, mg/L
COD_t	The temporally obtained COD at certain time, mg/L
m	The mass of adsorbent, g
v	The volume of wastewater for each batch (100 mL)

References

[1] PCBS, Economic Statistics, Industrial Survey, Palestine, 2006.

[2] Bharati, S., Shete, P., Shinkar, S., Comparative study of various treatments for dairy industry, IOSR Journal of Engineering (IOSRJEN), 2013.

[3] Devi, M.G., Dumaran, J., and Feroz, S., Dairy wastewater treatment using low molecular weight crab shell chitosan, Journal of The Institution of Engineers (India), 2012.

[4] Kushwaha, J.P., Srivastava, C., and Mall, I., Treatment of dairy wastewater by commercial activated carbon and bagasse fly ash: parametric, kinetic and equilibrium modelling, disposal studies, Bioresource Technology, 2010.

[5] Wang, R., Tsang, C., Olds, E., Weber, P., Utilizing acid mine drainage sludge and coal fly ash for phosphate removal from dairy wastewater, Environmental Technology, 2013.

[6] Sivakumar, D., and Christyno, E., Isotherm studies on dairy industry wastewater using neem leaves powder, Automation and Autonomous System, 2012.

[7] Al-Jabari, M., Aqraa, F., Shahin, S., and Khatib, A., The treatment of chromium tanning wastewater using natural marl, Journal of the Argentine Chemical Society, 2009.

[8] Al-Jabari, M., Aqra, F., Shahin, S., and Khatib, A., Monitoring chromium content in tannery wastewater, Chemical Speciation and Bioavailability, 2009.

[9] Ho, Y.S., Review of second-order models for adsorption systems, .J. Hazard Mater, 136 (3), 2006.

[10] Elagroudy, S., El-Gohary, F., Microwave Pre-treatment of Mixed Sludge for Anaerobic Digestion Enhancement, Int. J. of Thermal & Environmental Engineering, Vo. 5, No. 2, 2013.

[11] Qiu, H., Lv, L., Pan, B.C., Zhang, Q.J., Zhang, W.M., Zhang, Q.X., Critical review in adsorption kinetic models. J. Zhejiang Univ. Sci. A 10, 716–724, 2009.

[12] Al-Jabari, M., Kinetic mass transfer adsorption model for treating dairy wastewater with stone cutting solid waste, Environmental Technology and Innovation, 7, 21–29, 2017.

[13] Al-Jabari, M., Kinetic models for adsorption on mineral particles comparison between Langmuir kinetics and mass transfer, Environmental Technology and Innovation, 6, 27–37, 2016.

[14] Al-Jabari, M., Zahdeh, Z., Iqefan, N., Dweik, H., Technical feasibility of treating dairy wastewater with natural low cost adsorbents, EWDR Conference, Istanbul, Turkey, 2015.

[15] Al-Jabari, M., Abualfailat, M., and Shaheen, S, Treating leather tanning wastewater with stone cutting solid waste, Clean – Soil, Air, Water, 2012.

[16] Al-Jabari, M., Iqefan, N., Zahdeh, N., Dweik, H.,Adsorption of organic pollutants from dairy wastewater on soil: pollution problem and control, Int. J. Global Environmental Issues, Vol. 16, Nos. 1/2/3, 2017.

[17] Clesceri, L., Greenberg, A., Eaton, A., Standard methods for the examination of water and wastewater, 20th Edition, APHA American Public Health Association, 1998.

[18] Murali, K., Karuppia, K., Nithish, M., Kumar, S., and Raja, V., COD reduction using low cost bio sorbent, 2013.

[19] Largitte, L., Pasquier, R., A review of the kinetics adsorption models and their application to the adsorption of lead by an activated carbon, Chemical Engineering Research and Design, 2016.