UDK 678.7:544.723
Professional article/Strokovni članek

ISSN 1580-2949
MTAEC9, 47(4)525(2013)

RECYCLED POLYMER/CLAY COMPOSITES FOR HEAVY-METALS ADSORPTION

RECIKLIRAN KOMPOZIT POLIMER-GLINA ZA ADSORPCIJO TEŽKIH KOVIN

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Prejem rokopisa – received: 2012-09-26; sprejem za objavo – accepted for publication: 2012-11-27

Post-consumer plastics in the form of disposable cutlery, plates, cups, and containers for dairy products that are made of polystyrene (PS) were used to formulate polymer/clay composite materials for the purpose of using them as an adsorbent for the removal of heavy metals from waste water. The clay used in this study was a natural clay obtained from the Tabuk region in the north of Saudi Arabia. The composites were formulated by mixing 5–10 % mass fractions of clay with PS in the molten state using conventional polymer-processing equipment. Composites of virgin PS and clay were also formulated in order to compare their ability to adsorb heavy metals with that of the recycled composites. The results showed that composites based on recycled PS have a good adsorption capability in comparison with those of the virgin composites. For example, the amount of lead adsorbed per gram of adsorbent was tripled when using composites containing only 5 % of clay and 95 % of recycled PS in comparison with those with virgin PS.

Keywords: clay, polystyrene, recycled PS, heavy metals

Iz odpadne potrošniške plastike v obliki jedilnega pribora za enkratno uporabo: krožnikov, skodelic in embalaže za mlečne proizvode, iz polistirena (PS), je bil pripravljen kompozitni material polimer-glina kot adsorbent za odstranitev težkih kovin iz odpadne vode. Glina, uporabljena v tej študiji, je naravna glina, pridobljena iz območja Tabuk na severu Savdske Arabije. Kompoziti so bili izdelani z mešanjem masnih deležev 5–10 % gline s PS v staljenem stanju s konvencionalno opremo za predelavo polimerov. Za primerjavo zmožnosti adsorpcije težkih kovin so bili izdelani kompoziti z deviškim PS in glino ter reciklirani kompoziti. Rezultati so pokazali, da imajo kompoziti na osnovi recikliranega PS večjo vpojno zmogljivost v primerjavi z deviškim kompozitom. Na primer, količina adsorbiranega svinca na gram adsorbenta se je v primerjavi z deviškim PS pri uporabi kompozita s 5 % gline in 95 % recikliranega PS potrojila.

Ključne besede: glina, polistiren, reciklirani PS, težke kovine

1 INTRODUCTION

Waste water including heavy metals is an inimitable class of waste water, with all heavy metals being toxic pollutants. Lead ions in waste water, for example, is a pollutant and dangerous to human and water environments. As a result, it is necessary to eliminate heavy metals from the waste water before discharging it into the environment. The removal of heavy metals from aqueous solutions may be achieved by applying several physical and chemical methods, such as ion exchange, extraction, flotation, coagulation, electro-deposition and precipitation. However, most of these methods are considered non-viable due to the cost factor. Various materials have been utilized for heavy-metals removal from waste water include activated carbon, lime and bio-sorbents.[1] For the large-scale treatment of waste water for heavy-metals removal we need to look for a low-cost material as an alternative, cost-effective adsorbent for the removal of heavy metals such as lead ions from waste water.

Polymeric adsorbents may be used in the adsorption of heavy metals because of their easy regeneration and strong mechanical properties in comparison with other adsorbents such as activated carbon, cellulose and silica gel.[2] For example, CHA-111 AND MCH-111 polymeric adsorbents were used as perfect adsorbents for adsorption pollutants such as phenols from waste water.[3–5] Despite the fact that polymers are preferably utilized to adsorb heavy-metal ions, the higher costs of these materials may hinder their employment as cost-effective adsorbents for the large-scale production of heavy-metal free water.

In this work we tried to look for low-cost adsorbents for the removal of lead from waste water by choosing two discarded materials that can be obtained with no cost. These two materials were natural clay and discarded post-consumer polystyrene. In our previous publication[6] we proved that natural clay taken from the north of Saudi Arabia may be used as a cost-effective adsorbent for lead ions. In the current work, we report on the formulation of clay with post-consumer polystyrene articles that are eventually discarded in landfills as waste materials. Recycled polystyrene/clay composite material for the purpose of using it as an adsorbent for heavy-metals removal from waste water was formulated by the current research. The clay used in this study was a natural clay obtained from the Tabuk region in the north of Saudi Arabia. The composites were formulated by mixing the mass fractions 5–10 % of clay with polystyrene (PS) in the molten state using conventional polymer-processing equipment. Composites of virgin PS and clay were also formulated in order to compare their ability to adsorb heavy metals with that of the recycled composites. The adsorption isotherms of the two polymer composites are also discussed here and the equilibrium parameters required to design a batch absorber are also estimated.

2 EXPERIMENTAL

2.1 Materials

The polymers used in this study were virgin polystyrene and recycled polystyrene. The virgin polystyrene was supplied by the SABIC Company in Saudi Arabia, while the recycled polystyrene was post-consumer plastics in the form of disposable cutlery, plates, cups, and containers for dairy products that are made of polystyrene. A lead-ion solution was prepared from lead nitrate purified LR [$Pb(NO_3)_2$] and was supplied by S.define- Limited (Laboratory Rasayan).

2.2 Preparation of the polymer composites

The thermoplastic polymer is polystyrene (PS). Polystyrene has a suitable affinity for clay particles and is readily melt processed using conventional techniques such as internal mixing and extrusion. The polymer can be a so-called "virgin" polymer, i.e., a newly formed polymer, or it can be derived from polymer scrap, such as recycled polymer, as it permits the reuse of polymer materials which might otherwise be discarded, necessitating disposal in a landfill or similar.

The clay material was milled to a size below about 100 mesh and then washed with distilled water several times to remove the impurities. The clay was then dried in a vacuum oven overnight. The dried clay was then dry mixed with polymer particles, and an emulsifier, alkyltrimethyl-ammonium, was incorporated to ease the dispersion of the clay in the polymer matrix. The composites were formulated by mixing 5–10 % of clay with PS in the molten state using a dynisco mini extruder (LME) at a temperature above the melting or softening point of the polystyrene, above about 180 °C. The extrudate was collected in a water bath, dried and subsequently ground to granules of different sieve sizes, ranging from 0.5 mm to about 3 mm.

2.3 Scanning Probe Microscopy

The morphology of the neat PS and the prepared PS/clay composites was visualized using a scanning probe microscope (SPM); solver next (NT-MDT).

2.4 Adsorption Isotherm

Stock lead solutions with a concentration of 1000 μg/g were diluted to the required concentrations (50–1300 μg/g), and then used in the equilibrium experiments. After that, the initial concentration of the lead ion samples and the final concentration for these samples were diluted and analyzed by atomic absorption spectroscopy (model AAnalyst 700, PerkinElmer). The adsorption isotherm experiments were performed by placing a constant mass of polymer composite (1 g) in 50 ml of lead-ion solution in glass bottles in a constant agitation shaker. In each isotherm run, the temperature used was 20 °C and the particle size was 0.5 mm. The adsorption process reached equilibrium after 30 min; however, the equilibrium experiments were conducted for 3 hours to insure that the equilibrium state was attained. The samples were then filtered using filter papers, diluted, and the concentrations were measured. The adsorbed concentration was calculated from the mass-balance equation on the batch absorber as follows:

$$q_e = V(C_o - C_e)/M \quad (1)$$

where M indicates the adsorbent mass, V is the solution volume, q_e is the adsorbed lead-ions concentration in mg/g, C_o is the initial concentration of lead ions and C_e is the lead ions concentration in the bulk solution at equilibrium. The amount of lead ions adsorbed on the adsorbent versus the lead ions equilibrium concentration in the solution can be plotted to obtain the equilibrium adsorption isotherm curve and the maximum capacity of the adsorption of lead ions by the polymer composites. The spent adsorbents, polymer/clay composites, may be regenerated by treating with strong acids such as hydrochloric acid (HCl).

3 RESULTS AND DISCUSSION

The amount of lead adsorbed on polystyrene/clay composites, virgin and recycled, versus the lead concentration in the solution was plotted to obtain the equilibrium adsorption isotherm curves for the two composite systems. This is shown in **Figures 1** and **2**. As a first observation we can see from **Figures 1** and **2** that the adsorption capacities for such composite systems are low. Here we have polystyrene as the major phase that is a non-polar polymer with no functional groups on the surface and hence its activity towards lead ions adsorption may be attributed to other factors other than its surface functionality. Surface morphologies in the form of the rough topology of the polystyrene granules used in the adsorption isotherm experiments may be responsible for such performance. Another explanation for the adsorption of lead ions on the polystyrene is that, the lead ions may be adsorbed by the polystyrene with van der Waals forces because of the adsorption of the lead ions on the polymer is of the Langmuir monolayer type. The same trend was observed by Zhang,[7] where he attributed the adsorption to the monolayer adsorption in addition to the capillary condensation and micropore filling.

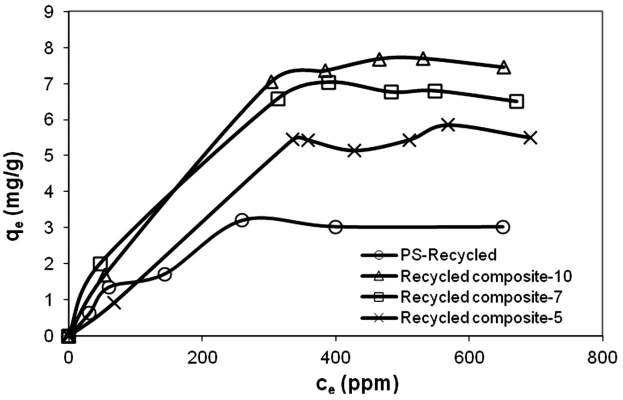

Figure 1: Equilibrium isotherm experiments for the adsorption of lead ions on the recycled polymer/clay composites with different amounts of clay in mass fractions: 5 %, 7 % and 10 %

Slika 1: Ravnotežne izoterme za adsorpcijo ionov svinca na recikliranem kompozitu polimer-glina z različno vsebnostjo gline v masnih deležih: 5 %, 7 % in 10 %

It is clear from **Figures 1** and **2** that composites based on recycled PS have a good adsorption ability in comparison with those of the virgin composites. For example, the amount of lead adsorbed per gram of adsorbent was tripled when using composites containing only 5 % of clay and 95 % of recycled PS in comparison with those containing virgin PS. The adsorption behavior of the neat recycled and virgin PS is also shown in **Figures 1** and **2** in order to compare their adsorption ability with those reinforced with clay particles. Needless to say that the adsorption capacity of neat clay, that is Tabuk clay in this study, is much higher than that of the composite system.[6]

The maximum capacity for the adsorption of lead ions on the recycled polymer composite was on recycled polymer-10, as shown in **Figure 1**. It is clear that recycled polymer-10 was more efficient in terms of lead adsorption when compared with that of the other types of recycled polymers (recycled polymer-5 and recycled polymer-7). The polar groups (such as carbonyl and hydroxyl) that may exist on the surfaces of a recycled polymer from exposure to the sun may enhance the adsorption of metals ions. The surface of a recycled polymer material may play an important role in adsorption of the adsorbate, where it has many different polar groups, such as carbonyl and hydroxyl.[8] **Figure 3** shows that the recycled composites have a distinct peak of IR at a wave number of between 1700 and 1800, which is an indication of the presence of a carbonyl group. In addition, the mixed clay plays another role in enhancing the adsorption of the lead ions on the recycled polymer composite.

In contrast to what is seen with the recycled composites, the neat virgin PS behaves better in terms of adsorption capacity in comparison with that of the virgin composites, especially at a low clay content, from 5–7 %. This may be attributed to diminishing the role of the clay particles in the absence of a functional group on the PS surface. It should also be noted that, as shown in **Figure 2**, the maximum capacity of the adsorption of lead ions on the virgin polymer composite, was less than that of the recycled composites. **Figure 4** shows the appearance of the neat PS and the composite surfaces taken by the SPM. It is clear that while the neat PS surface appears relatively smooth, the clay particles were not dispersed well within the virgin PS matrix, as shown in **Figure 4b**. In contrast, the clay particles were dispersed evenly in the recycled PS matrix, as shown in **Figure 4c**. This may be due to the help of the carbonyl group on the recycled PS surface.

Two isotherm models – Langmuir and Freundlich – were applied to describe the experimental data for the polymer composites used in this study.

The Langmuir model suggests that the adsorption of heavy-metal ions on the adsorbent surface is a monolayer and this is applied to evaluate the maximum capacity of the adsorption.[7] The Langmuir isotherm model is written as follows:

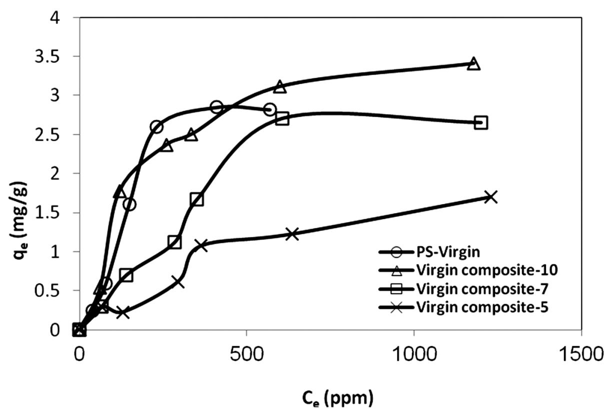

Figure 2: Equilibrium isotherm experiments for the adsorption of lead ions on the virgin polymer/clay composites with different amounts of clay in mass fractions: 5 %, 7 % and 10 %

Slika 2: Ravnotežne izoterme za adsorpcijo ionov svinca v deviškem kompozitu polimer-glina z različno vsebnostjo gline v masnih deležih: 5 %, 7 % in 10 %

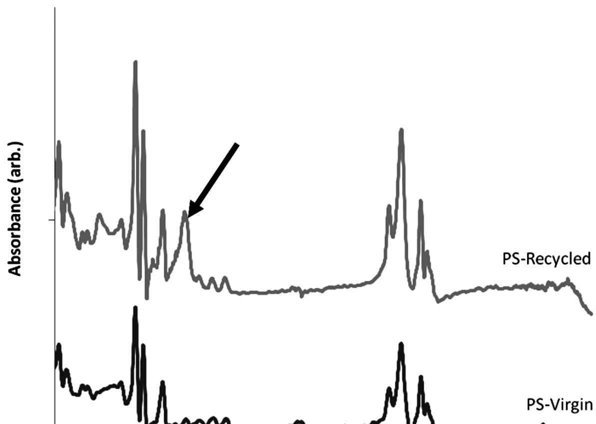

Figure 3: FTIR comparison of virgin and recycled PS

Slika 3: FTIR-primerjava deviškega in recikliranega PS

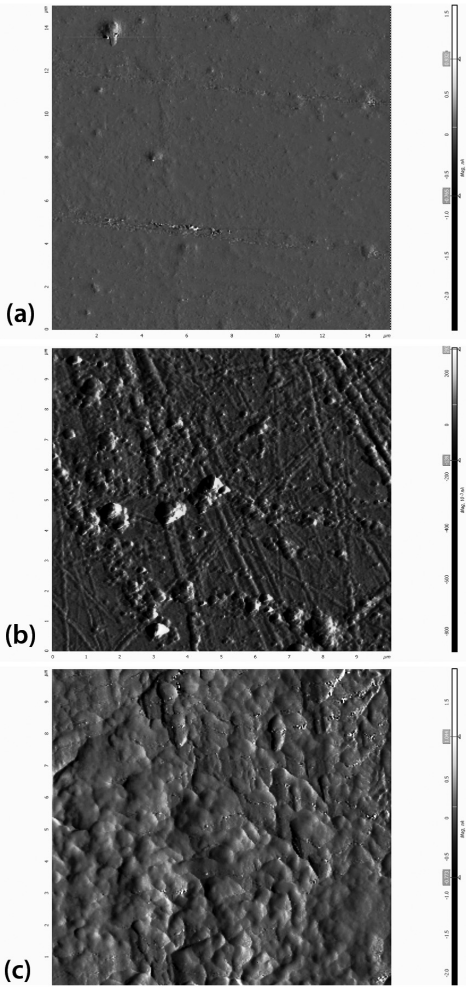

Figure 4: SPM graphs of PS/clay composites: a) neat PS; b) virgin composites; c) recycled composites

Slika 4: SPM-posnetki kompozita polimer-glina: a) gladek PS; b) deviški kompozit; c) recikliran kompozit

Table 1: Langmuir constants for the lead-ions adsorption on the recycled polymer/clay composites

Tabela 1: Langmuirova konstanta za adsorpcijo ionov svinca na recikliranem kompozitu polimer-glina

Material	K/(l/g)	b/(l/mg)	R^2
Recycled composite-5	0.1845	0.0316	0.9788
Recycled composite-7	7.880	1.1844	0.9833
Recycled composite-10	0.1629	0.0198	0.9862

$$q_e = \frac{KC_e}{1+bC_e} \quad (2)$$

where k and b are constants. The mathematical forms of the Langmuir model in the linear form is given below:

$$C_e/q_e = 1/K + (b/K)C_e \quad (3)$$

The Langmuir parameters K and b may be obtained by using the linear regression technique with equation 3. **Figures 5** and **6** show the linear relationship between C_e/q_e and C_e for the polymer composites, recycled and virgin. The equilibrium parameters K and b are listed in **Tables 1** and **2**.

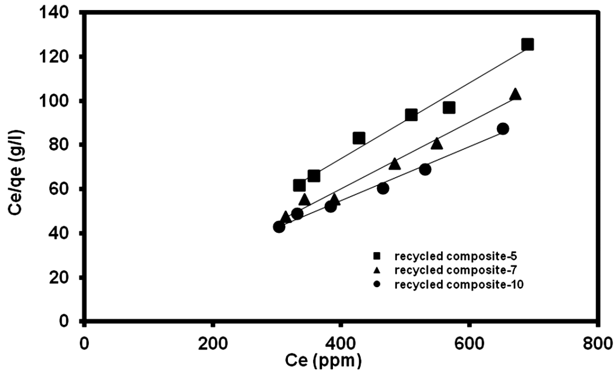

Figure 5: Langmuir isotherm fit for the experimental data of recycled polymer composites

Slika 5: Ujemanje Langmuirove izoterme z eksperimentalnimi podatki za kompozite iz recikliranega polimera

Table 2: Langmuir constants for the lead-ions adsorption on the virgin polymer/clay composites

Tabela 2: Langmuirova konstanta za adsorpcijo ionov svinca na deviškem kompozitu polimer-glina

Material	K/(l/g)	b/(l/mg)	R^2
Virgin composite-5	0.005	0.0020	0.9838
Virgin composite-7	0.008	0.0019	0.8828
Virgin composite-10	0.023	0.0060	0.9988

The Freundlich isotherm model may be used to describe the adsorption isotherm of heterogeneous adsorption surfaces. The model is given by the following relation:

$$q_e = K_f \, C_e^{(1/n)} \quad (4)$$

The model, given by eq. 4, may be written in linear form as follows:

$$\lg q_e = \lg K_f + (1/n) \lg C_e \quad (5)$$

The equilibrium constants K_f and n may be calculated using the linear regression technique with equation 5.

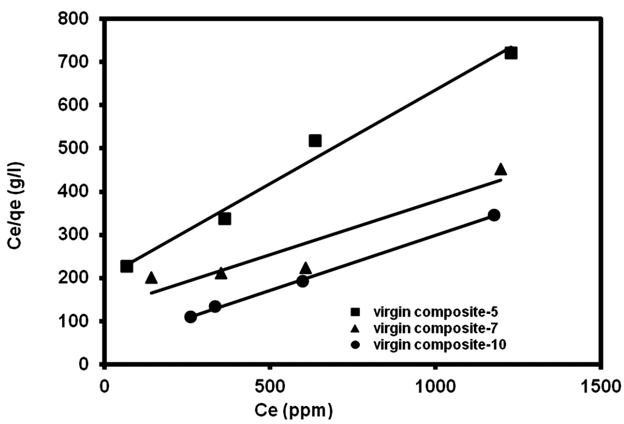

Figure 6: Langmuir isotherm fit for the experimental data of the virgin polymer composites

Slika 6: Ujemanje Langmuirove izoterme z eksperimentalnimi podatki za kompozite iz deviškega polimera

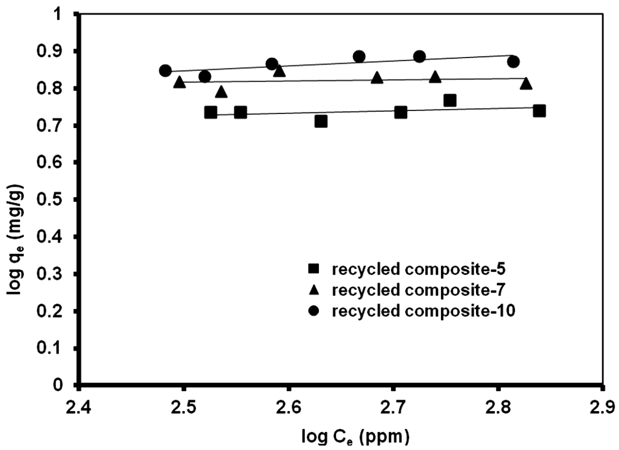

Figure 7: Freundlich isotherm fit for the experimental data of the recycled polymer composites
Slika 7: Ujemanje Freundlichove izoterme z eksperimentalnimi podatki za kompozite iz recikliranega polimera

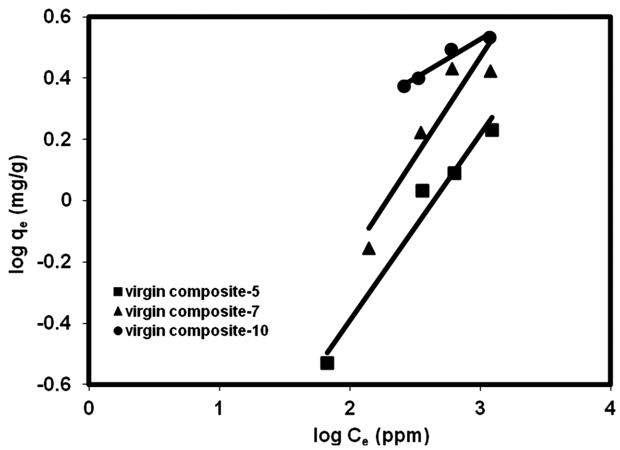

Figure 8: Freundlich isotherm is used to fit the experimental data of the virgin polymer composites
Slika 8: Ujemanje Freundlichove izoterme z eksperimentalnimi podatki za kompozite iz deviškega polimera

When the value of n is greater than one, this may indicate that the adsorption of lead ions by the polymer is favorable.[9] **Figures 7** and **8** demonstrate the linear relationship between lg q_e and lg C_e for the polymer composite systems employed in this study. The equilibrium constants, K_f and n, are presented in **Tables 3** and **4**.

Table 3: Freundlich constants for the lead-ions adsorption on the recycled polymer/clay composites
Tabela 3: Freundlichova konstanta za adsorpcijo ionov svinca na recikliranem kompozitu polimer-glina

Material	K_f/(l/g)	n	R^2
Recycled composite-5	3.77	16.584	0.1679
Recycled composite-7	5.59	35.587	0.0341
Recycled composite-10	3.39	7.855	0.5564

Table 4: Freundlich constants for the lead-ions adsorption on the virgin polymer/clay composites
Tabela 4: Freundlichova konstanta za adsorpcijo ionov svinca na deviškem kompozitu polimer-glina

Material	K_f/(l/g)	n	R^2
Virgin composite-5	0.0245	1.641	0.9712
Virgin composite-7	0.0319	1.528	0.8787
Virgin composite-10	0.5869	3.959	0.9558

The data represented by **Figures 5** to **8** and **Tables 1** to **4** show that both models describe the experimental data well, except in the case of the recycled composites data fitted to Freundlich model, as seen from **Table 3**, where the values of R^2 are extremely low.

4 CONCLUSIONS

The results from the adsorption isotherm showed that the recycled polymer composites were more efficient than the virgin polymer composites. This may be attributed to the functional groups, such as the carbonyl that may exist on the surfaces of a recycled polymer, i.e., the PS, from a prolonged exposure to sunlight. In addition, the clay mixed with the recycled polymer plays another role in enhancing the adsorption of the lead ions on the recycled polymer composites. The presence of the carbonyl group on PS surface may contribute to a better dispersion of the clay particles in the PS matrix. The results also showed the recycled polymer composites have an acceptable adsorption capacity for the lead ions compared to the virgin composites. This finding could be an advantage when it comes to utilizing plastic waste for waste water treatment.

The experimental data were fitted using Langmuir and Freundlich models. Both models used were effective in describing the experimental data, except for the data for the recycled composites that was fitted to the Freundlich model.

Acknowledgments

The authors thank the King Abdulaziz City for Science and Technology for providing the support for this study.

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