

Removal of aliphatic organic acids from the wastewater by using adsorbents obtained from buffalo droppings

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ABSTRACT

The buffalo droppings were chemically modified with acids and bases, and characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy, surface area, and Fourier-transform infrared spectroscopy analysis. The raw and treated dropping samples were then used as adsorbents for the removal of aliphatic organic acids including formic acid, acetic acid and propanoic acid from their aqueous solutions. The adsorption was studied at different temperatures, that is, 20°C, 30°C, and 40°C, and different time durations ranging from 0.5 to 8 h. The adsorption kinetics was investigated and various thermodynamic parameters were determined such as activation energy, free energy, enthalpy, and entropy, etc. The results were also interpreted using different adsorption models including Bhangham, Elovich, and intraparticle diffusion.

Keywords: Temperature; Buffalo dropping; Organic acids; Adsorbents; Kinetics

1. Introduction

Water pollution is a major challenge for environmentalists worldwide, the main factors responsible for which are industries, agricultural development and population explosion [1]. These activities continuously pollute the water reservoirs such as lakes, rivers, oceans, and groundwater, and render it as a health risk for all the living organisms around the globe [2]. Out of different contaminants, the aliphatic organic acids are of great concern with health risk. Various types of aliphatic organic acids are released by petrochemical, fine chemical and the industries using organic acids as a reagent including beverage, pharmaceuticals, cosmetics, food preservatives, detergent, textile printing, ink, photographic chemicals, dyes, pesticides, rubber, and plastics industries. These organic acids are harmful to

plants and animals in high concentrations. In animals these acids may cause various problems like diarrhea, stomach pain and the burning of mouth and throat, therefore proper disposal or treatment of water containing aliphatic organic acids is an important issue [3–5]. Various techniques such as electrochemical technique [6] used to treat the organic and inorganic pollutants from the wastewater include ion exchange, evaporation, precipitation, reverse osmosis, liquid extraction, distillation, bipolar membrane electro-dialysis and reactive distillation [3]. However, most of these techniques are very expensive, particularly when the quantity of water to be treated is very large. Alternately, adsorption is the only process [7], which has more attraction because of its high efficiency, low cost, simple operation, high range of recovery, specific selectivity and recyclability [8]. Generally, during the adsorption process, the microporous adsorbent

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retains the contaminants by chemical bonds, ion exchange and physical attractive forces [9,10]. In literature, the adsorbents used for the removal of the organic acids from the contaminated water include, mineral clays [11], activated carbon, biomass, etc. [1,12].

In the present work, we have used (excrements) the chemically modified buffalo droppings as potential adsorbents for the removal of organic acid from wastewater. The composition of animal dropping is about 80% water and undigested plant material which contains nutrients, that is, about 0.8% k, 0.4% Na, 2.4% Ca, 0.7% P, and 0.8% Mg and some microorganisms. 2.5 to 4.0% of nitrogen is present in dung; 10%–20% of nitrogen is present in the form of bacteria [13–15]. Generally, millions of tons of animal dungs are produced annually, out of which the production rate of the buffalo dung is 12.20 kg animal⁻¹ d⁻¹, cow dung is 11.6 kg animal⁻¹ d⁻¹ and that of goat dung is 0.70 kg animal⁻¹ d⁻¹. A large number of animal droppings are produced per day, therefore its proper management is needed, otherwise, the disposal of such large amount of agriculture and animal waste will produce severe environmental problems [16], like the generation of bad odor, microbes, greenhouse gases and particulate matter which strongly affect human's health. People living near animal dropping suffer from respiratory, cardiac and psychological disorders. The use of dung as fuel produces the greenhouse and toxic gases which is more dangerous than the gases produces from modern coal-burning plants. Hence the present study addresses the use of animal droppings as a low-cost bio-sorbent for the elimination of aliphatic organic acids from aqueous solutions. The adsorption kinetics and different adsorption models are also investigated for the adsorption process.

2. Experimental setup

2.1. Preparation of treated buffalo dropping sample

Dropping of buffalo were collected and dried in the laboratory. The dried mass was ground to powder and screened through a mesh. A quantity of 100 g of raw powder was added to about a solution of 0.5 N HCl and HNO₃ in the ratio of 1:1 and stirred for a few hours. The content of the beaker was filtered and washed with doubly distilled water until the material was free of acid and neutralized. Then the sample was treated with 500 ml of 2.0 N NaOH solution for 24 h in a beaker. The content of the beaker was filtered and washed with doubly distilled water till neutralization. The treated sample was dried at 100°C for 24 h and was cooled in a desiccator for 24 h. Both the samples were stored in a glass bottle for further study.

2.2. Characterization of adsorbent

2.2.1. Surface area

The surface area of samples was analyzed using the Brunauer–Emmett–Teller (BET)-N₂ sorption method. The experiment was conducted at -196°C using pore size and surface area analyzer (Model: Quantachrome NOVA 2200, USA). The surface area was determined under standard conditions. DR method was used for pore size distribution using Nova Win2 data analysis software.

2.2.2. Fourier-transform infrared spectroscopy

The transmission infrared spectrum of buffalo dropping was recorded by using Shimadzu 8201PC (Made of Japan) Fourier-transform infrared (FT-IR) spectrophotometer and FTCOM-1 computer control disc unit. The sample was mixed with KBr in 1:1 ratio and hard-pressed under a load of 10 torr for 4–6 min in a hydraulic press to obtain 0.5 mm thick pellets. The disc was dried in a vacuum oven at 110°C and 10 torr pressure. After drying for 12 h all the water molecules were removed from the pellets. The pellet was mounted on the sample and the FT-IR transmission bands of buffalo and dropping were found in the region of 500–4,500 cm⁻¹.

2.2.3. Scanning electron microscopy

The surface morphology of the dry powder sample of buffalo dropping was studied by scanning electron microscopic technique using a scanning electron microscope (SEM)-Model-JSM-5910, JEOL (Japan). The sample was mounted on aluminum disc (1 cm × 0.25 cm) to record the SEM micrographs. The detection of metals was carried out by an energy-dispersive X-ray spectroscopy (EDS) technique using EDS-INCA 200 Oxford Instruments (Origin is United Kingdom).

2.2.4. Moisture contents studied

1 g of the sample was taken a pre-weighed china dish and placed in the oven, with the temperature maintained at 105°C ± 1°C for 2 h. The sample was cooled in the desiccator and then weighed. The % moisture was calculated from the weight loss on heating by using the following formula:

$$\text{Moisture contents (\%)} = \frac{\text{weight loss during heating}}{\text{weight of sample}} \times 100 \quad (1)$$

2.2.5. Ash contents

To calculate the ash content take one gram ground sample of buffalo droppings and ignite it under 600°C in a furnace using porcelain crucibles. For suitable circulation of air, the door of the furnace was kept partially open until the sample was burned, the crucible was allowed to cool for some time and then put it in a desiccator. The weight of this crucible was determined. This procedure was repeated thrice until we get a constant equilibrium weight. To calculate the % weight loss the following formula was used:

$$\text{Ash contents (\%)} = \frac{\text{weight of ash}}{\text{weight of sample}} \times 100 \quad (2)$$

2.3. Preparation of acid solutions

0.1 M stock solutions of formic acid, acetic acid, and propanoic acid were prepared. Then dissolving the known amounts of acid in double-distilled water in a beaker. The next step diluted these solutions of acids to 1 L in volumetric flasks with double distilled water. The stock solutions of acids were then standardized with standard NaOH

solution. Working standards of these acids were prepared after standardization with NaOH from stock solutions of acids by the dilution method.

2.4. Adsorption study

Sorption of organic acids (formic acid, acetic acid, and propanoic acid) was studied using Batch adsorption techniques. 0.2 g of adsorbent powder of buffalo sample was taken in 250 ml reagent glass bottles, each containing 20 ml aliphatic organic acid (formic acid, acetic acid, and propanoic acid) solution. The bottles were placed in thermostat Shaker and were shaken for different intervals. After completion of the reaction, the adsorbent was filtered through Wattman No. 3 filter papers, the filtered was stored for the determination of the concentration of acids.

The adsorption experiments were carried out at a different temperature to study the kinetics of the adsorption. The amount adsorbed (mol g^{-1}) has calculated by using the following formula:

$$C_{\omega} = \left[\frac{(C_0 - C_v)}{W} \right] \times V \quad (3)$$

where C_0 is initial concentration in (mol ml), C_v is the equilibrium concentration (mol ml), C_{ω} is the amount adsorbed (mol g^{-1}), and V is the volume of adsorbate in ml and W is the amount of adsorbent in g.

2.5. Determination of acids concentration

The concentration of acetic acid, propionic acid and formic acid in the treated water was determined by titration against standard NaOH solution, using phenolphthalein indicator. In a typical procedure known quantity of acid solution was taken in the conical flask. Two to three drops of phenolphthalein indicator were added to the conical flask. The solution was then titrated against standard NaOH solution. The amount of acid in solution was calculated from the volume of NaOH solution used from a burette.

3. Results and discussions

3.1. Characterization of adsorbent

Raw and treated samples of buffalo dropping were characterized by BET surface area, SEM, EDS, and FT-IR technique for surface functional groups.

BET method was used to determine the surface area of powdered buffalo dropping. It is based on multilayer adsorption of N_2 gas on the adsorbent surface and provides a base to explore the microporous surface area of adsorbent. This technique is based on monolayer adsorption of Langmuir theory leading to multilayer adsorption. Eq. (4) is a linear form of the BET equation and was used to determine the surface area.

$$\frac{1}{v \left[\left(\frac{P_0}{P} \right) - 1 \right]} = \frac{C-1}{v_m C} \left(\frac{P}{P_0} \right) + \frac{1}{v_m C} \quad (4)$$

where v is the weight of gas adsorbed at a relative pressure, P/P_0 and v_m is the weight of adsorbate forming a monolayer on the surface of the adsorbent. C is called BET constant and is related to the energy of the 1st adsorbed layer and its value indicates the extent of adsorbate and adsorbent interaction. From the plot of $1/v \left((P_0/P) - 1 \right)$ against P/P_0 the surface area of the samples was determined. Results are given in Table 1, which shows that surface area for the raw and treated buffalo droppings was 215 and 455 $\text{m}^2 \text{g}^{-1}$ respectively. These results indicate that the surface area of the powdered samples has increased by acid and alkali treatment [16]. It is obvious that during the chemical treatment, HCl and NaOH, dissolved away the extraneous mineral materials from the surface of the materials, due to which the pores are exposed leading to increase in the surface area, or it may also be due to leaching of the cations [17].

The surface morphology and the elemental composition of buffalo dropping samples before and after chemical treatment were studied by SEM and EDS analysis. The micrographs of the adsorbent samples are given in Figs. 1a and b. The micrograph of the raw samples (before chemical treatment) shows irregular surfaces with some cavities and disintegrated particles on the surface. The micrograph of the treated sample shows a layered surface with uniform pleats and channels. The EDS results of the raw and treated samples are given in Figs. 2a and b and Table 2. It can be seen from the data that major elements found in the raw samples include C, O, and Si, whereas other elements present in small concentration are Al, P, Mg, Cl, and K. In case of treated samples the elements found were C, O Si, and Ca. These results show that during the chemical treatment the most of the extraneous mineral materials have been eliminated [17].

FT-IR spectra of both raw and treated buffalo samples are given in (Fig. 3). The peak in the region from 1,000 to 1,250 cm^{-1} shows the presence of C–H bond stretching. This band was present only in treated buffalo dropping samples. Both buffalo dropping samples also show C=C stretching which indicates the presence of aromatic ring while in case of raw buffalo dropping sample S=O was also detected which indicates the presence of oxygen-containing functional groups. The FT-IR spectra of treated dropping shows the presence of C–H bond stretching and the spectra of the raw sample shows the presence of both C–H and C=C bond stretching [18–20].

4.2. Adsorption studies

4.2.1. Adsorption kinetics and equilibration time

Equilibration time for the adsorption of aliphatic organic acids (formic acid, acetic acid, and propanoic acid) onto dry dropping powder of buffalo was studied for a period of

Table 1
BET surface area of animal droppings sample

BET surface area ($\text{m}^2 \text{g}^{-1}$)	
Raw sample	Treated sample
215	455

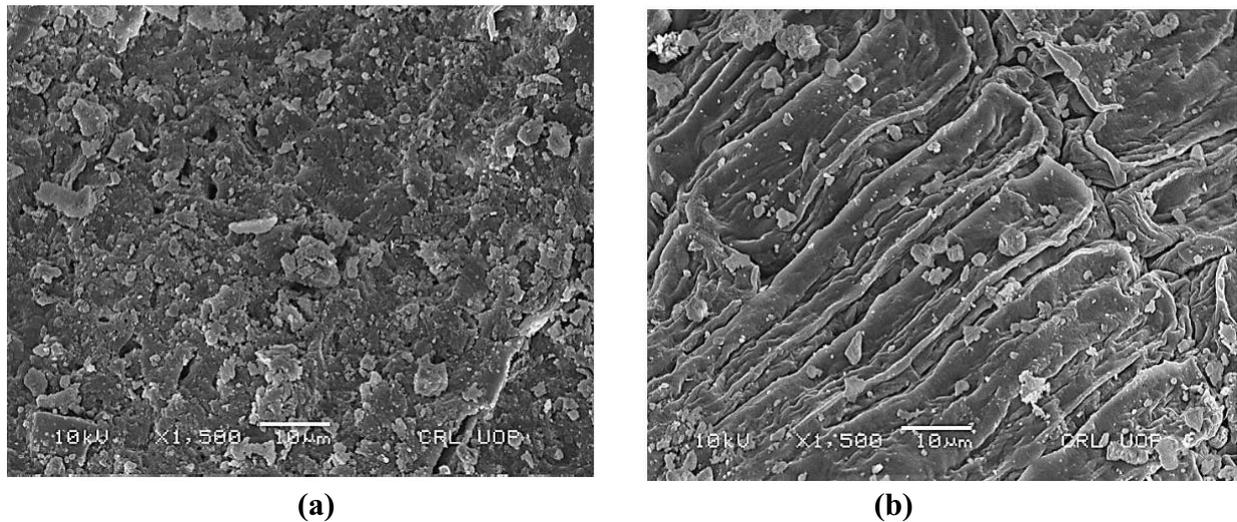


Fig. 1. SEM images of buffalo droppings (a) raw dropping and (b) treated dropping.

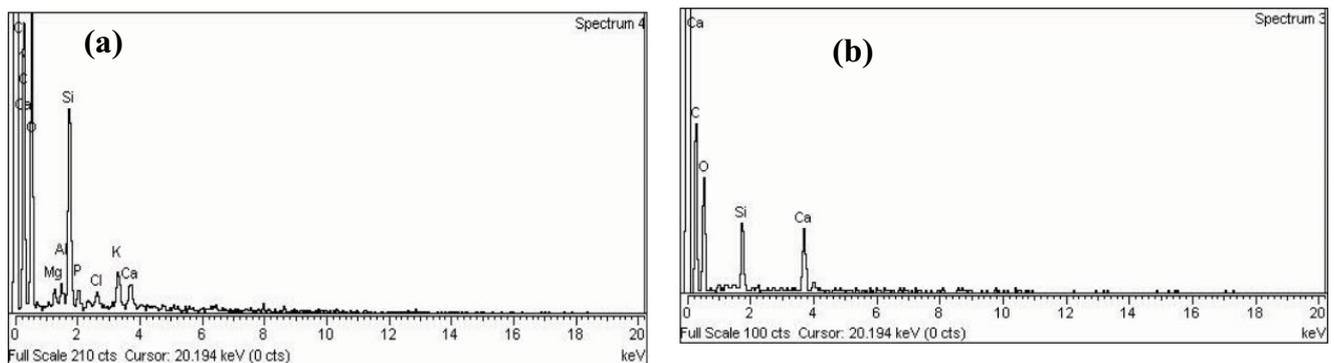


Fig. 2. EDS profiles of buffalo droppings (a) raw dropping and (b) treated dropping.

Table 2
Elemental composition of raw and treated buffalo dropping samples obtained by EDS analysis

Elements	Raw sample Weight %	Atomic %	Treated sample Weight %	Atomic %
C	48.89	58.05	44.33	54.02
O	42.54	37.92	45.6	41.72
Mg	0.54	0.32	–	–
Al	0.37	0.19	–	–
Si	4.60	2.33	3.72	1.94
P	0.54	0.25	–	–
Cl	0.42	0.17	–	–
K	1.18	0.43	–	–
Ca	0.92	0.33	6.36	2.32

0.5–8 h (i.e. 0.5, 1, 2, 4, 6, and 8 h) at 25°C. Figs. 4a–c illustrates that the equilibrium was reached up to 2 h and then become a plateau. Equilibrium time study shows that optimum time for the surface coverage is 2 h. After Equilibration time study adsorption kinetics were studied, the adsorption of acids (formic acid, acetic acid, and propanoic acid) were studied

at 20°C, 30°C and 40°C on raw and treated buffalo dropping samples shown in Figs. 4a–c. It was concluded that in the first 15 min the adsorption was fast and then slowly decreased owing to the maximum surface coverage. When the adsorption temperature was increased sorption of acid (formic acid, acetic acid, and propanoic acid) on buffalo dropping sample

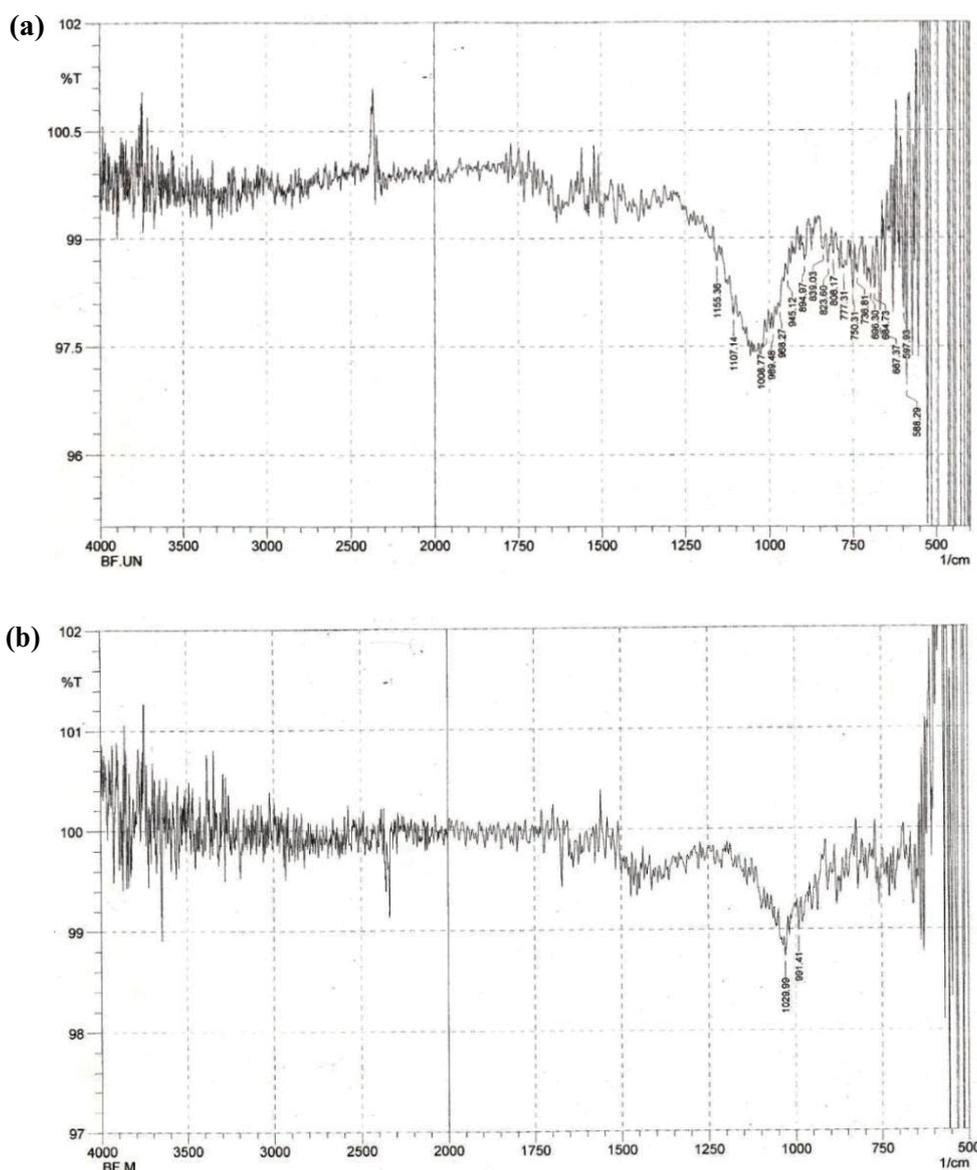


Fig. 3. FT-IR spectra of raw (a) treated buffalo and (b) droppings.

was also increased which indicates that the process is endothermic. Adsorption also showed an increase as we go from formic acid to propanoic acid. This is according to Traub's rule which states that adsorption will increase as the homologous series increase [21].

4.2.2. Adsorption kinetics linear equations

From the adsorption of aliphatic organic acids (formic acid, acetic acid, and propanoic acid) on buffalo dropping sample first-order rate equation was used to determine the rate constant in the following equation [22].

$$\ln C_v = \ln C_0 - K_{ad} t \quad (5)$$

C_v is equilibrium concentration and C_0 is the initial concentration of acid (mol/ml) and K_{ad} is the rate constant. The rate

constant was calculated from the plot of $\ln C_v$ vs. t , the results are given in Table 3. The rise in the rate constant by increasing the reaction temperature was clear from the tables. According to the first-order rate equation, the R^2 value was close to 1, which shows the greatest harmony with the literature.

Arrhenius equation was used for the determination of activation energies, which is given below:

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \quad (6)$$

E_a stands for activation energy, k_1 and k_2 indicate rate constants and T represents temperature. The activation energies for the adsorption of organic acids (formic acid, acetic acid, and propanoic acid) onto raw and treated buffalo dropping samples are given in Table 3. The sequence

Table 3
Thermodynamic constants for adsorption of aliphatic organic acid onto animals dropping samples

Buffalo	k (min ⁻¹)			ΔE^*	ΔH^* (kJ mol ⁻¹)			ΔS^* (J mol ⁻¹ K ⁻¹)		
Dropping	20°C	30°C	40°C	(kJ mol ⁻¹)	20°C	30°C	40°C	20°C	30°C	40°C
Sample										
Formic acid										
Treated	0.005	0.005	0.006	9.806	7.370	7.287	7.204	-0.299	-0.300	-0.299
Raw	0.002	0.002	0.002	8.717	5.890	5.807	5.724	-0.311	-0.312	-0.312
Acetic acid										
Treated	0.006	0.006	0.008	16.087	13.652	13.568	13.485	-0.275	-0.277	-0.276
Raw	0.002	0.002	0.002	10.708	8.272	8.189	8.106	-0.304	-0.305	-0.304
Propanoic acid										
Treated	0.004	0.004	0.007	21.865	19.430	19.347	19.264	-0.259	-0.261	-0.279
Raw	0.002	0.002	0.002	4.912	2.476	2.393	2.310	-0.324	-0.324	-0.325

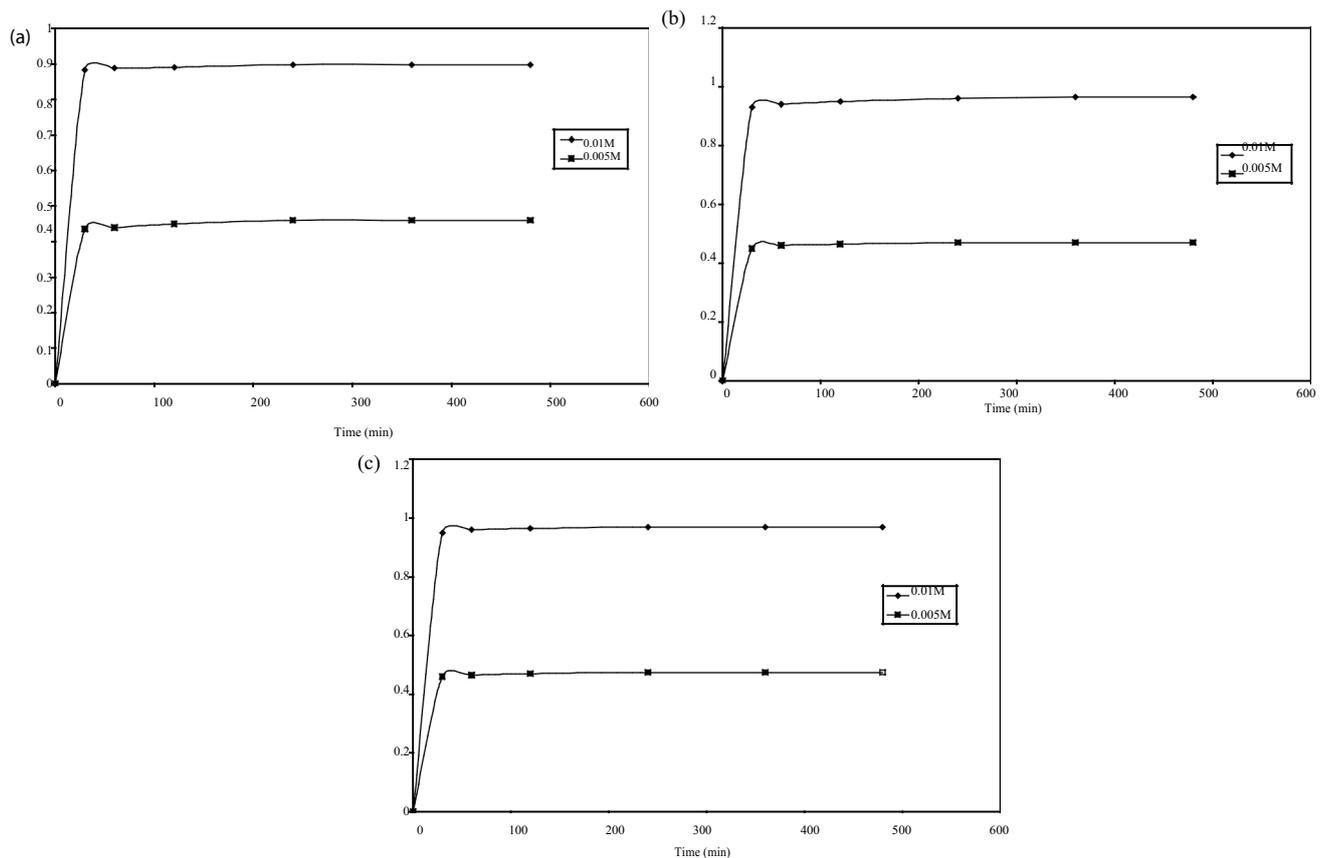


Fig. 4. Equilibration time for the adsorption of acids of buffalo dropping sample (a) formic acid, (b) acetic acid, and (c) propanoic acid.

of activation energies for the adsorption of acids on buffalo droppings is as, in case of formic acid the activation energies were 9.81 kJ mol⁻¹ for treated buffalo dropping and 8.71 kJ mol⁻¹ for raw dropping sample. In the case of acetic acid, the activation energy was 16.08 kJ mol⁻¹ for a treated

sample and 10.71 kJ mol⁻¹ for raw buffalo dropping sample. Similarly the activation energies in the case of propanoic acid, it was 21.87 kJ mol⁻¹ for a treated sample and 4.91 kJ mol⁻¹ for raw buffalo dropping sample. From these results, it is clear that the treated sample shows an increase in activation

energy. From activation energy, the free energy ΔE^\ddagger and different thermodynamic parameters like (ΔH) enthalpy and (ΔS) entropy were calculated; results are shown in Table 3. Enthalpy and entropy were calculated using the following equations [22].

$$\Delta H^\ddagger = \Delta E^\ddagger - RT \quad (7)$$

$$\Delta S^\ddagger = R \left[\ln \frac{k_b h}{k_B T} + \frac{\Delta H^\ddagger}{RT} \right] \quad (8)$$

In these equations k_b , h , k_B are the rate constant, plank constant and Boltzmann constant respectively. The calculated values of enthalpy (ΔH) for the adsorption of acids on raw and treated buffalo dropping samples are given in Table 3. From the table, it is clear that enthalpy has a positive value for all the adsorbents. Enthalpy (ΔH) gives positive values which indicate that the adsorption process is endothermic in nature [23]. The entropy (ΔS) gave negative values, which show the affinities of acids to adhere on the surface of dropping, the value of entropy decrease when the adsorption temperature increases this indicate that the acid get a steady position on the dropping surface.

4.2.3. Elovich model

The linear form of Elovich model is given below [24]:

$$C_\infty = \frac{1}{A} \ln(BA) + \frac{1}{A} \ln(t) \quad (9)$$

A straight line with slope “1/A” and the intercept “1/A ln(BA)” was obtained when C_∞ was plotted against $\ln(t)$, as shown in Fig. 5. In most of the cases, “A” value decreases from 20°C into 40°C in (g mg^{-1}) which indicates that the optimum condition for the adsorption was high temperature (Figs. 5a–c). The R^2 values which are closer to 1 show that the model is best fitted to the process of adsorption of acids onto the surface of droppings.

4.2.4. Bhangham equation

Bhangham equation is expressed in a linear form as below:

$$\log \log \frac{C_0}{C_0 - C_v W} = \log \frac{k_0 W}{2.303 V} + a \log t \quad (10)$$

where C_0 is the initial concentration of acid, W indicates the weight of adsorbent, V shows the volume of solution,

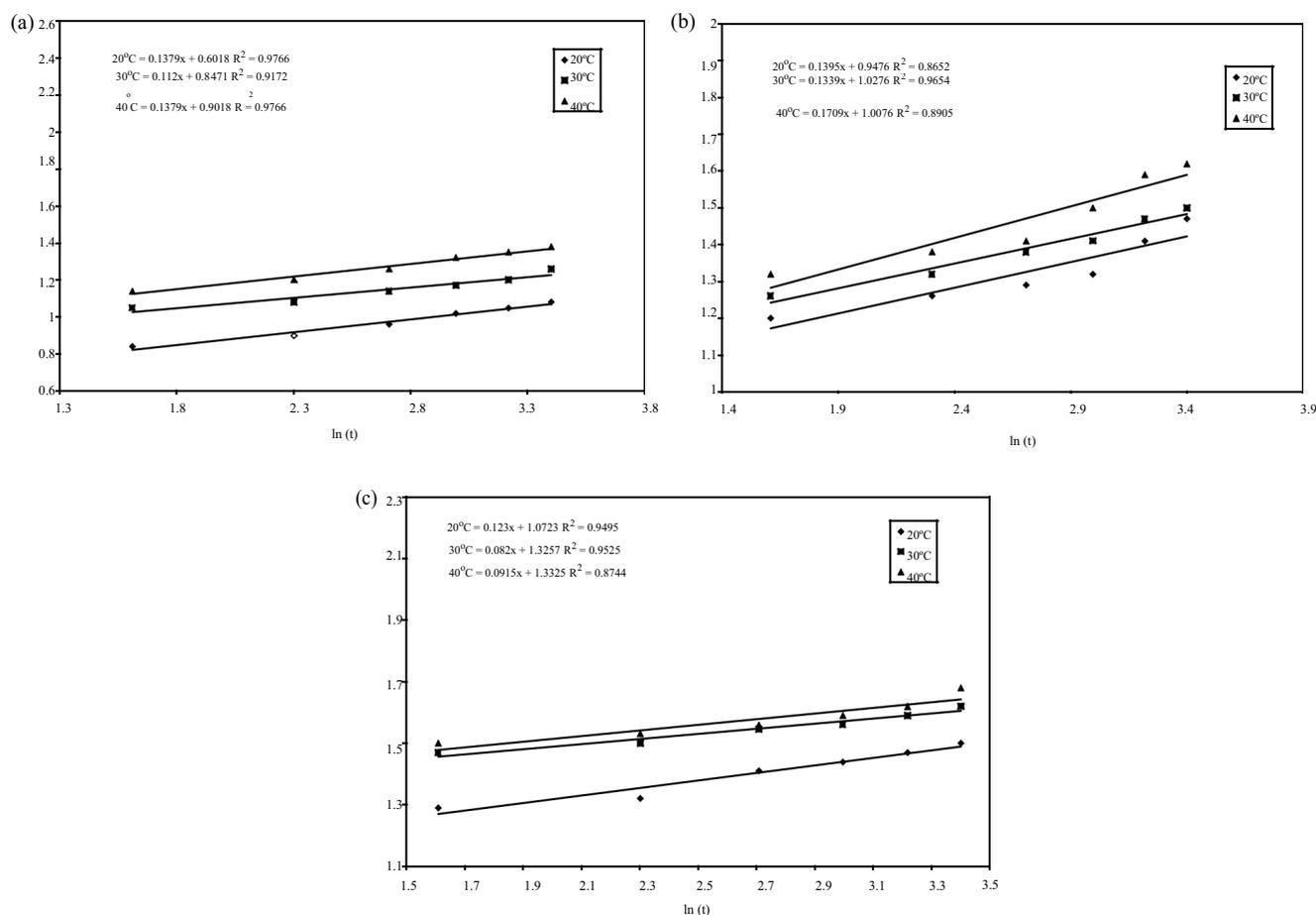


Fig. 5. Elovich plot for the adsorption of organic acids on treated buffalo dropping sample (a) formic acid, (b) acetic acid, and (c) propanoic acid.

the quantity adsorbed at time t is C_v . Using the slope and intercept of linear plots shown in Figs. 6a–c, values of k_0 and A were calculated Tables 4a and b. When the shaking temperature increases the value of A decreases, and the value of k_0 is increased, which shows that the allocation of acids onto pores of dropping is a significant and well-inhibited process [25,26].

4.2.5. Parabolic diffusion model (intraparticle diffusion)

It is evident from the literature reports [24] the plot of C_ω vs. $t^{1/2}$ indicates multi-linearity which characterizes various steps included in the adsorption. Weber and Morris stated that intraparticle diffusion is distinct from the following equation [27].

$$C_\omega = K_{\text{kid}} t^{1/2} + B \quad (11)$$

The K_{kid} value was obtained by plotting C_ω vs. $t^{1/2}$, the values of the intraparticle diffusion coefficient (kid) are given in Tables 4a and b. The kid values in case formic acid at 40°C were 0.04 for raw buffalo dropping sample which is <0.08 of treated buffalo dropping sample. The kid value for acetic acid at 40°C was 0.0414 for raw buffalo dropping sample

which is <0.10 of the treated sample, similarly, the kid value for propanoic acid at 40°C was 0.03 for raw buffalo dropping sample which is <0.05 of treated buffalo dropping sample.

Propionic acid has a higher diffusion coefficient as compared to acetic acid which has a higher diffusion coefficient when compared to formic acid. The R^2 (correlation coefficient) for parabolic diffusion is closer to 1, which shows that acid adsorption onto droppings occur in large amount. This is owing to the immediate action of most easily available adsorbing sites on the sorbent surface [26,27].

4. Conclusion

Treated and raw dropping samples of buffalo were characterized by BET surface area, SEM, EDS and FT-IR technique for surface functional groups. The surface areas of raw and treated samples were found to be 215 to 455 $\text{m}^2 \text{g}^{-1}$. The SEM shows that the surface of the material carries pores in different shapes and size. The EDS analysis indicated that the samples contain carbon, oxygen, silicon, calcium and some other metals in minor quantities. The FT-IR study indicates the presence of C–H, C=C and S=O functionalities in the raw and treated buffalo dropping samples. The sorption of organic acid (formic acid, acetic acid, and propanoic acid) on each sample was studied by batch adsorption techniques at

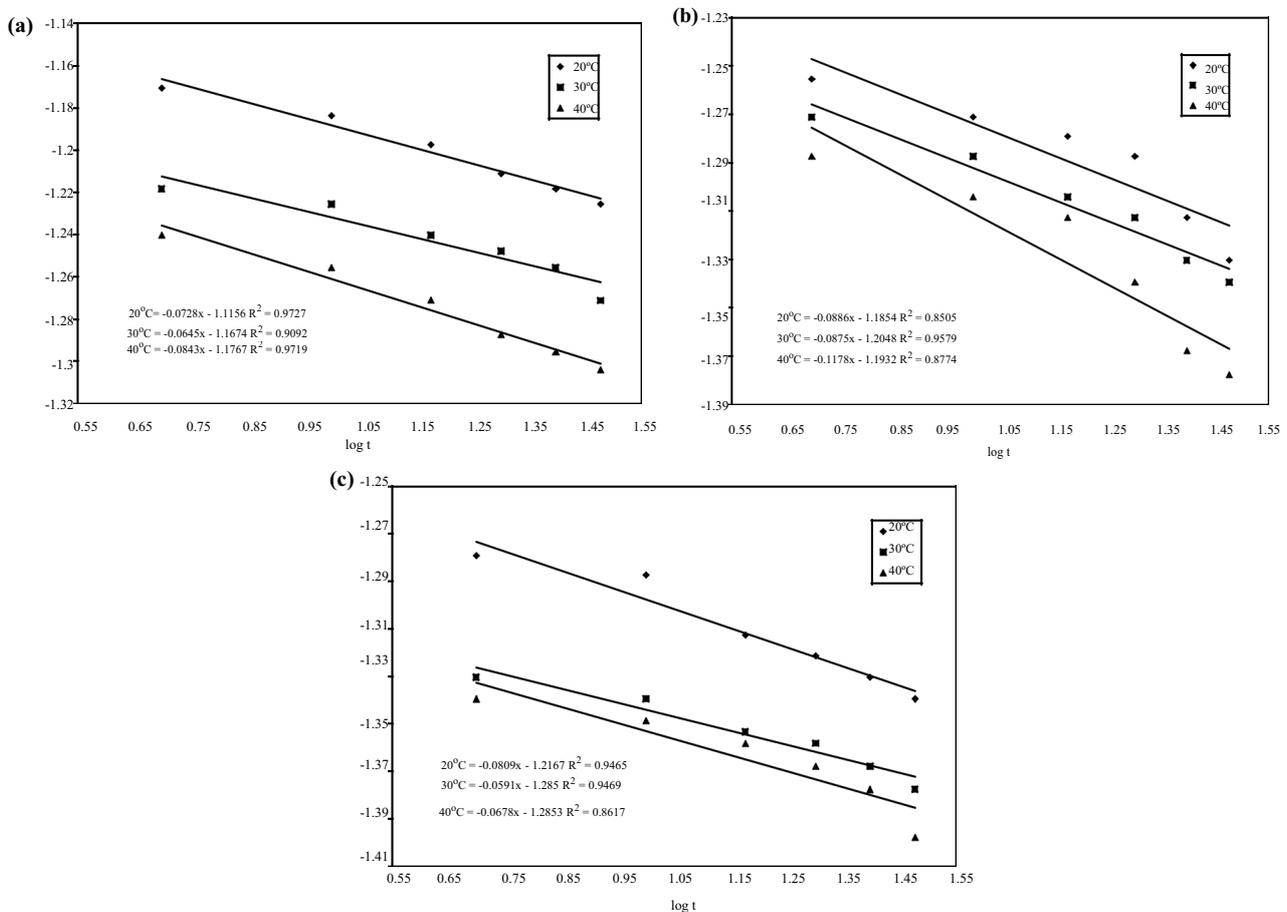


Fig. 6. Bhangham plots for the adsorption of organic acids on treated buffalo dropping sample (a) formic acid, (b) acetic acid, and (c) propanoic acid.

Table 4a
Comparison of the parameters of rate equations for organic acid onto treated buffalo dropping sample

Temperature	Elovich		Intraparticle diffusion			Bhangham		
	A_E (g mg ⁻¹)	R^2	C (mg g ⁻¹)	K_{id} (mg g ⁻¹ min ^{-1/2})	R^2	A	KO	R^2
Formic acid								
20°C	7.2516	0.9766	0.6654	0.0767	0.9943	-0.0728	17.6479	0.9727
30°C	8.9285	0.9172	0.894	0.0634	0.9686	-0.0645	15.6627	0.9092
40°C	7.2516	0.9766	0.9654	0.0767	0.9943	-0.0843	15.3311	0.9719
Acetic acid								
20°C	7.1684	0.8652	1.0031	0.0797	0.931	-0.0886	15.0271	0.8505
30°C	7.46825	0.9654	1.0877	0.0749	0.9933	-0.0875	14.3707	0.9579
40°C	5.8513	0.8905	1.0771	0.0973	0.9508	-0.1178	14.7599	0.8774
Propanoic acid								
20°C	8.13008	0.9495	1.1283	0.0685	0.9713	-0.0809	13.9827	0.9465
30°C	12.1951	0.9525	1.3619	0.046	0.9867	-0.0591	11.9496	0.9469
40°C	10.929	0.8744	1.3689	0.0523	0.9415	-0.0678	11.9388	0.8617

Table 4b
Comparison of the parameters of rate equations for organic acid on raw buffalo dropping sample

Temperature	Elovich		Intraparticle diffusion			Bhangham		
	A_E (g mg ⁻¹)	R^2	C (mg g ⁻¹)	K_{id} (mg g ⁻¹ min ^{-1/2})	R^2	A	KO	R^2
Formic acid								
20°C	16.2601	0.8888	0.2154	0.035	0.9481	-0.0256	20.7678	0.9062
30°C	13.7931	0.9605	0.2671	0.0403	0.9803	-0.0309	20.4359	0.9585
40°C	13.7931	0.9605	0.3271	0.0403	0.9803	-0.0316	19.9477	0.9585
Formic acid								
20°C	17.452	0.8854	0.3404	0.0326	0.9442	-0.0249	19.742	0.8828
30°C	16.9491	0.9173	0.3644	0.0316	0.9444	-0.0242	19.5384	0.8817
40°C	13.6986	0.8731	0.3503	0.0414	0.9262	-0.0322	19.7374	0.8669
Propionic acid								
20°C	14.4928	0.9766	0.3927	0.0383	0.9943	-0.0307	19.3996	0.975
30°C	17.0358	0.9895	0.439	0.0325	0.9949	-0.03	19.1907	0.996
40°C	19.5313	0.9139	0.4677	0.0291	0.9684	-0.0232	18.6936	0.9119

different temperatures (20°C, 30°C, and 40°C). The adsorption of organic acid on the dropping samples from the aqueous solutions showed that the equilibrium is attained in 2 h for complete surface coverage. The adsorption of acids was found to follow the adsorption first-order kinetics. The Bhangham, Elovich and parabolic equations were found to apply to the results of the adsorption.

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