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Removal of formaldehyde from aqueous solution by adsorption on kaolin and bentonite: a comparative study

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Abstract

The adsorption of formaldehyde on bentonite and kaolin was studied in batch mode. Parameters like adsorbent dose, pH, contact time and agitation speed were investigated. Langmuir, Freundlich and Temkin isotherms were employed for describing adsorption equilibrium. The maximum amounts of formaldehyde adsorbed (q_{max}), as evaluated by Langmuir isotherm, were 3.41 and 5.03 milligrams per gram of ground kaolin and bentonite, respectively. The study results led to the conclusion that kaolin and bentonite, vastly available inorganic clays, have good potential as adsorbents to remove toxic organic pollutants such as formaldehyde from water.

Key Words: Adsorption, formaldehyde, isotherms, kaolin, bentonite

1. Introduction

Water resources including fresh water are of great importance for natural ecosystems as well as human development but they are becoming limited due to the increasing population, urbanization, and climate changes. This scarcity is basically due to water pollution, which is caused by the discharge of untreated or partially treated industrial effluents into the natural ecosystem, posing serious problems it. Thus these industrial effluents, containing a number of organic and inorganic chemicals as phenols, formaldehyde, dyes, and heavy metals, are major water pollutants (Bhole et al., 2004, Arellano-Cárdenas et al., 2005).

Formaldehyde is an organic chemical that is very prevalent in the environment and it ranks top in the list of environmental impacts of among 45 chemical products (Oliveira et al., 2004). It can have a toxic, allergenic, and carcinogenic impact on humans (Moustafa et al., 2002; Weng et al., 2009). It is an environmental toxicant that causes adverse effects on the health of living organisms and is one of the major pollutants emitted from both industrial and non-industrial facilities. Point sources that release formaldehyde into the environment include textile, paper, leather, photographic, pharmaceutical, and plastic industries along with adhesive and resin manufacturing and disinfectant producing units (Vidal et al., 1999; Campos et al., 2003; Oliveira et al.,

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2004). Formaldehyde remains of concern as the major indoor air pollutant and a number of methods have been adopted for the adsorption of gaseous formaldehyde.

Adsorbents utilized in this regard include activated carbon, aluminum oxide, ceramic material impregnated with potassium permanganate etc. (Sekine and Nishimura, 2001). Little attention has been paid to the removal of this organic pollutant from industrial effluents or waste water. Adsorption has been recognized as an efficient technology for the removal of a number of organic and inorganic pollutants and involves the phase transfer of adsorbate molecules onto the adsorbent, leaving the clear effluent behind (Salman et al., 2011). Activated carbon generated by microorganisms has been utilized for the removal of formaldehyde from industrial effluents (Hidalgo et al., 2002). However, the use of activated carbon as an adsorbent is limited, especially in developing countries because of its relatively high cost and the difficulties with its regeneration (Pollard et al., 1992).

In the present work formaldehyde was removed using 2 different adsorbents, i.e. kaolin and bentonite, and a comparative study of them was carried out. Kaolin, usually referred as china clay, is inorganic clay and contains 10%-95% of the mineral kaolinite. It is represented by the chemical formula $Al_2Si_2O_5(OH)_4$ and most often occurs as clay-sized, plate-like, hexagon crystals. It is a well-known low-cost raw clay and shows good adsorption properties (Vimonses et al., 2009). Bentonite is also an inorganic clay mainly composed of montmorillonite. It contains exchangeable inorganic cations (e.g., Na^+, Ca^{2+}, H^+) on the internal and external surfaces of montmorillonite that upon replacement with organic cations enhance the adsorption capacity for the removal of organic pollutants (Bartelt-Hunt et al., 2003; Akçay and Akçay, 2004; Özcan et al., 2005; Özacar and Şengil, 2006; Özcan et al., 2007). The present study includes the calculation of process parameters in addition to detailed study of Langmuir, Freundlich, and Temkin isotherm models. The equilibrium parameters, kinetics, and thermodynamics for the adsorption of formaldehyde from aqueous solution using 3 different adsorbents were also investigated.

2. Material and methods

2.1. Preparation of adsorbents

Kaolin and bentonite collected from local areas of Pakistan were ground to 60-70 micron (ASTM) particle size. The ground adsorbents were washed thoroughly with distilled water in order to remove any dissolved impurities and then dried at 110 °C. The dried adsorbents were used without any further chemical processing.

2.2. Stock solution and standards

Stock solution (1000 mg/L) of formaldehyde was prepared by using fixed aliquots of 37% formalin solution (Merck). Standard solutions of formaldehyde of preferred concentrations (5-25 mg/L) were prepared by successive dilutions of their respective stock solutions.

2.3. Equipment

A digital pH-meter (HANNA, Model-8417) was used for pH adjustments. The pH of solutions was maintained using HCl (0.1 M) and NaOH (0.1M) along with standard buffers. A Labomed UV/VIS spectrometer (Model-UVD-3500) was used to determine the concentrations of formaldehyde at 515 nm. An orbital shaker with time control (VORTEX Model-OSM-747) was used during the optimization of process parameters.

2.4. Formaldehyde estimation

A simple method for the determination of formaldehyde in aqueous solution was used along with some modifications (Tanenbaun and Bricker, 1951). Aliquots (1-5 mL) of diluted solution of formaldehyde (4 μg/L) were transferred to 25.0 mL flasks. To each was added 10 mL of phenylhydrazine hydrochloride solution (1%) followed by 1.0 mL of potassium ferricyanide solution (2%). After 5 min 4.0 mL of concentrated hydrochloric acid was added and the solution was left for another 5 min. Then the solution was diluted to the mark and the absorbance measured at 515 nm against a blank prepared in a similar way.

2.5. Study of process parameters

Using the initial concentration of 25 mg/L for formaldehyde, a set of experiments were performed to check the effects of various process parameters (adsorbent dose, time of contact, pH, and agitation speed) on formaldehyde adsorption. The effect of a certain parameter was studied by varying it gradually keeping all other parameters constant. After adsorption, the substances under observation were filtered and the filtrates were subjected to UV/VIS spectrometry for the analysis of formaldehyde concentration.

The effect of sorbent dose was calculated by changing the sorbent amount from 0.2 g/25 mL to 1.8 g/25 mL. pH was varied from 1 to 9 to investigate the optimum pH for metal adsorption. The effect of time and agitation speed on metal adsorption was studied under gradually varied conditions of 5-45 min and 50-250 rpm for contact time and agitation speed, respectively.

2.6. Study of adsorption isotherms

Working solutions of varying concentration (30, 40, 50, 60, 70, and 80 mg/L) of formaldehyde were prepared by successively diluting the stock solution. Adsorption of formaldehyde from all these solutions was carried out under the optimum conditions obtained from the study of process parameters. Langmuir (Eq. (1)), Freundlich (Eq. (2)), and Temkin (Eq. (3)) isotherms were plotted and their subsequent parameters were calculated from their particular plots.

3. Results and discussion

3.1. Effect of adsorbent dosage

The effect of kaolin and bentonite dose on formaldehyde removal was studied by varying the adsorbent amount from 0.2 to 1.8 g/25 mL of formaldehyde for a time interval of 10 min. The observed trend due to variation in kaolin and bentonite dose is illustrated in Figure 1. Maximum removal of formaldehyde was 83.76% and 89.48% for the dose of 1.0 g/25 mL for kaolin and 0.8 g/25 mL for bentonite, respectively. The increase in adsorption with the increase in adsorbent dose is due to the fact that more active sites are available for formaldehyde adsorption. It was also observed that after certain addition of dose the adsorption of formaldehyde decreases or remains constant with further increase in adsorbent dose, which indicated that the adsorption mechanism is reversible and that there exists chemical equilibrium between adsorbent and adsorbate.

3.2. Effect of pH and agitation speed

pH is considered an important parameter in adsorption studies as it controls the adsorption at the adsorbent-solution interface. It affects both the adsorbent and the formaldehyde present in the solution. Experiments were conducted varying the solution pH from 2 to 10 while the rest of the factors were kept constant. The maximum removal of formaldehyde was observed at low pH range 2-3 as illustrated in Figure 2. At basic pH (>7) formaldehyde adsorption becomes difficult due to the repulsion of the accumulation for negatively charged hydroxyl ions around the adsorbent surface, providing repulsive forces for the carbonyl group of formaldehyde. The reason for the maximum adsorption of formaldehyde at low pH is development of more attractive forces between adsorbent and formaldehyde due to the accumulation of positively charged hydrogen ions around the adsorbent surface. Therefore, it is concluded that the optimum pH range for the removal of formaldehyde from its aqueous solution should be maintained at 2-3.

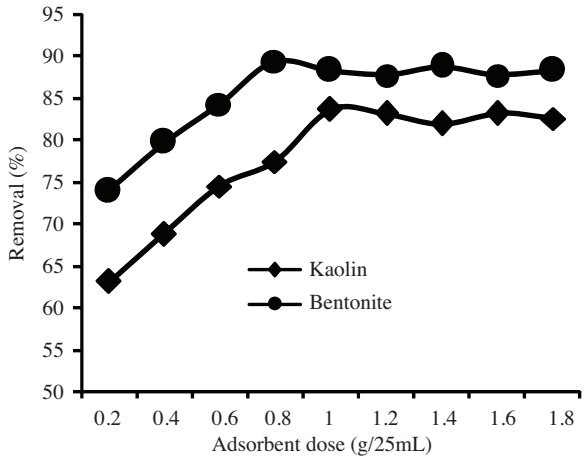

Figure 1. Effect of the adsorbent dose on adsorption of formaldehyde (formaldehyde concentration: 25 mg/L; contact time: 20 min; agitation speed: 125 rpm; temperature: 303 K).

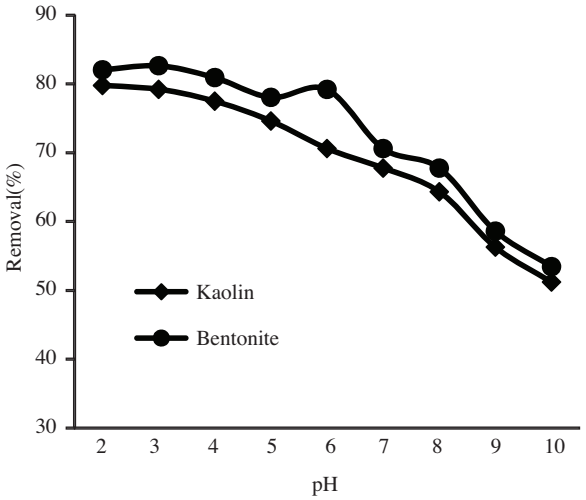

Figure 2. Effect of pH on adsorption of formaldehyde onto kaolin and bentonite (formaldehyde concentration: 25 mg/L; contact time: 20 min; agitation speed: 125 rpm; temperature: 303 K; dose: 1.0 g/25 mL for kaolin and 0.8 g/25 mL for bentonite).

Experiments were also conducted to check the effect of agitation speed on adsorption of formaldehyde and the results are shown in Figure 3. Optimum agitation speed for formaldehyde removal was found to be 125 rpm for both the adsorbents, i.e. kaolin and bentonite. This is because at very slow agitation speed the adsorbent accumulates at the bottom, reducing the contact surface area of the adsorbent with the adsorbate. Moreover, at very high speed, centrifugal forces operate, resulting in desorption of the adsorbate.

3.3. Effect of contact time

Contact time shows a marked influence on the adsorption efficiency and is used to elucidate the kinetics of the adsorption process. The effect of contact time on the percentage adsorption of formaldehyde indicated a sharp increase in adsorption within first 25 min for both adsorbents, i.e. kaolin and bentonite. A rapid increase in adsorption in less time revealed the physical nature of binding. No or a small increase in adsorption was observed after equilibrium was established. The observed trend is shown in Figure 4.

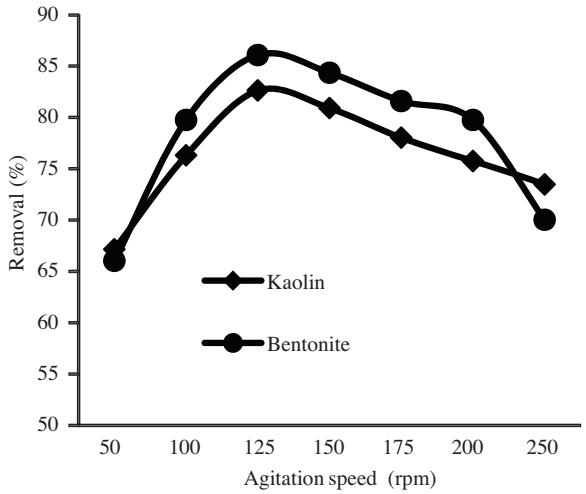

Figure 3. Effect of agitation speed on adsorption formaldehyde onto kaolin and bentonite (formaldehyde concentration: 25 mg/L; contact time: 20 min; temperature: 303 K; dose: 1.0 g/25 mL for kaolin and 0.8 g/25 mL for bentonite).

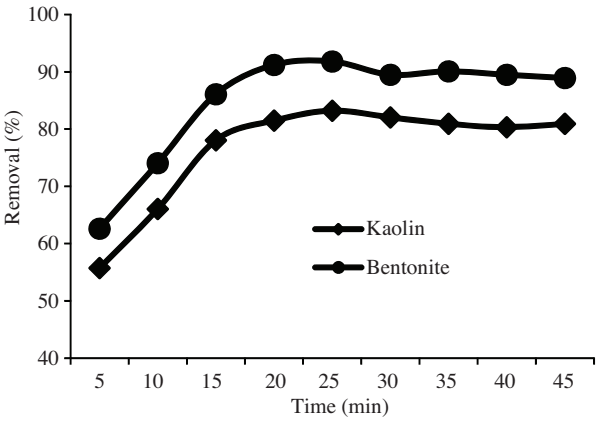

Figure 4. Effect of contact time on adsorption formaldehyde onto kaolin and bentonite (formaldehyde concentration: 25 mg/L; agitation speed: 125 rpm; temperature: 303 K; dose: 1.0 g/25 mL for kaolin and 0.8 g/25 mL for bentonite).

3.4. Adsorption isotherms

The adsorption mechanism and relationship between the concentration of the adsorbate and adsorption capacity of both the adsorbents were investigated using various adsorption isotherm models.

Langmuir (Eq. (1)), Freundlich (Eq. (2)), and Temkin (Eq. (3)) isotherms were used for the said purpose and their respective linear forms are as follows:

$$C_e/q_e = C_e/q_{\max} + 1/bq_{\max} \tag{1}$$

$$\log q_e = \log K_f + 1/n \log C_e \tag{2}$$

$$q_e = K_T \ln C_e + B_T \tag{3}$$

where 'q_e' and 'q_{max}' are the equilibrium and maximum uptake capacities (mg/g), respectively. 'b' is related to free energy of adsorption and represents the Langmuir adsorption constant. 'C_e' is the formaldehyde concentration in solution (mg/L) at equilibrium. 'K_f' is the Freundlich constant related to adsorption capacity (mg/g) while '1/n' represents the adsorption intensity. 'B_T' and 'K_T' are Temkin isotherm parameters; B_T (kJ/mol) is related to the heat of adsorption.

Isothermal studies were carried using varying initial concentrations of formaldehyde (10-60 mg/L) at optimum conditions. The equilibrium data were analyzed by regression analysis to evaluate the goodness of fit for Langmuir, Freundlich, and Temkin isotherm models. Adsorption isotherm parameters are illustrated in the Table for all the isotherm models calculated from their respective plot along with their correlation coefficients.

Table. Langmuir, Freundlich, and Temkin parameters.

Langmuir isotherm parameters				
Adsorbent	R^2 (Linear)	R^2 (Non-linear)	q_{max} (mg/g)	b (L/g)
Kaolin	0.995	0.9904	3.41	0.108
Bentonite	0.985	0.9947	5.03	0.099
Freundlich isotherm parameters				
Adsorbent	R^2		K_f	n
Kaolin	0.993		0.363	1.435
Bentonite	0.991		0.468	1.307
Temkin isotherm parameters				
Adsorbent	R^2		K_T	B_T (kJ/mol)
Kaolin	0.934		0.767	0.062
Bentonite	0.942		1.091	0.088

Monolayer coverage of adsorbate on the outer surface of the adsorbent is predicted by the Langmuir isotherm model (Theivarasu and Mylsamy, 2010). Correlation coefficients obtained for the linear Langmuir isotherm (Figure 5) using kaolin and bentonite were 0.995 and 0.985, respectively, showing the applicability of the Langmuir model to equilibrium data. Maximum uptake capacity for formaldehyde was 3.41 mg/g using kaolin as adsorbent, while in the case of bentonite it was 5.03 mg/g, which indicate that bentonite has a greater uptake capacity than kaolin. The non-linear Langmuir isotherm was also investigated (Figure 6). The non-linear regression analysis (R^2 value 0.9904 for kaolin and 0.9947 for bentonite) indicates that equilibrium data fits to the non-linear isotherm model.

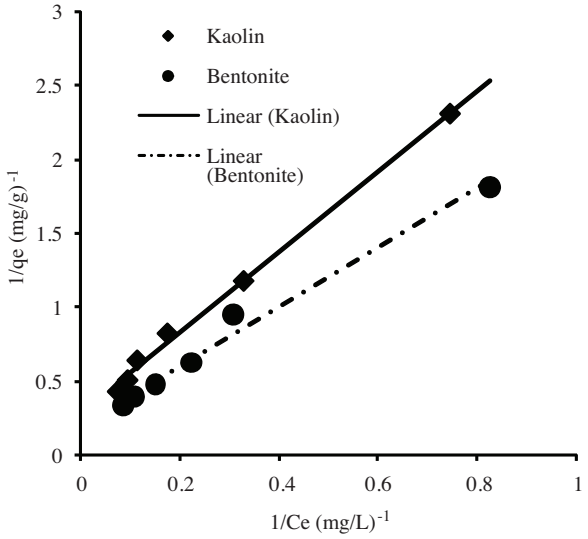

Figure 5. Linear Langmuir isotherm (formaldehyde concentration: 30-80 mg/L; agitation speed: 125 rpm; temperature: 303 K; dose: 1.0 g/25 mL for kaolin and 0.8 g/25 mL for bentonite).

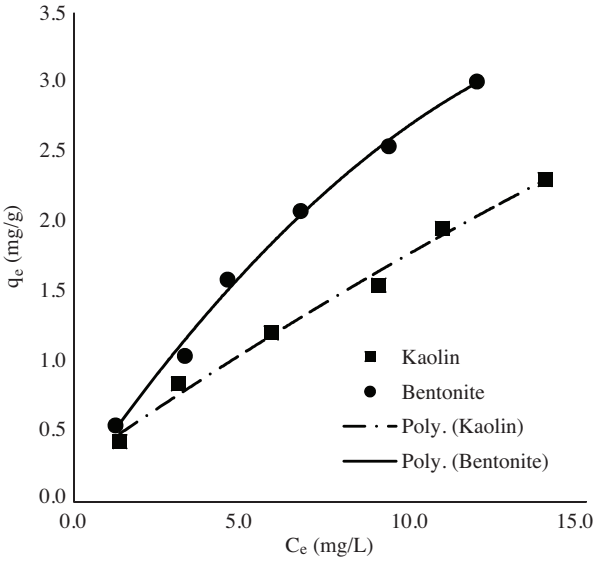

Figure 6. Non-Linear Langmuir isotherm (formaldehyde concentration: 30-80 mg/L; agitation speed: 125 rpm; temperature: 303 K; dose: 1.0 g/25 mL for kaolin and 0.8 g/25 mL for bentonite).

Freundlich model (Figure 7) was investigated for adsorption capacity (K_f) and adsorption intensity (n). K_f values as calculated from the intercept were 0.363 mg/g and 0.468 mg/g for kaolin and bentonite,

respectively, showing appreciable affinity for formaldehyde adsorption. The greater value of K_f for bentonite indicates the same trend as found in the Langmuir isotherm, i.e. bentonite is more effective for formaldehyde removal as compared to kaolin. 'n' value for adsorption of formaldehyde using kaolin and bentonite was 1.435 and 1.307, respectively. The value of n ranging from 1 to 10 shows favorable adsorption (Fan et al., 2008). Correlation coefficient values of 0.993 and 0.991 for kaolin and bentonite showed that the Freundlich model was more applicable to equilibrium data as compared to the linear Langmuir model, indicating multilayer formation on the heterogeneous surface of the adsorbent.

Temkin parameters 'K_T' and 'B_T' were calculated to study the adsorption potential and heat of adsorption. K_T values obtained from the Temkin isotherm model (Figure 8) were 0.767 and 1.091 for kaolin and bentonite, respectively, showing satisfactory adsorption potential for formaldehyde. The B_T values for kaolin and bentonite, 0.062 kJ/mol and 0.088 kJ/mol (less than 8), represent weak interaction between formaldehyde and adsorbents, indicating that the process would be physicosorption (Theivarasu and Mylsamy, 2010).

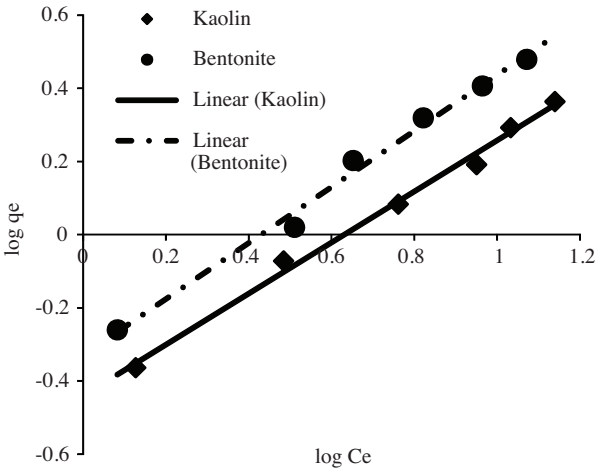

Figure 7. Frendlich isotherm (formaldehyde concentration: 30-80 mg/L; agitation speed: 125 rpm; temperature: 303 K; dose: 1.0 g/25 mL for kaolin and 0.8 g/25 mL for bentonite).

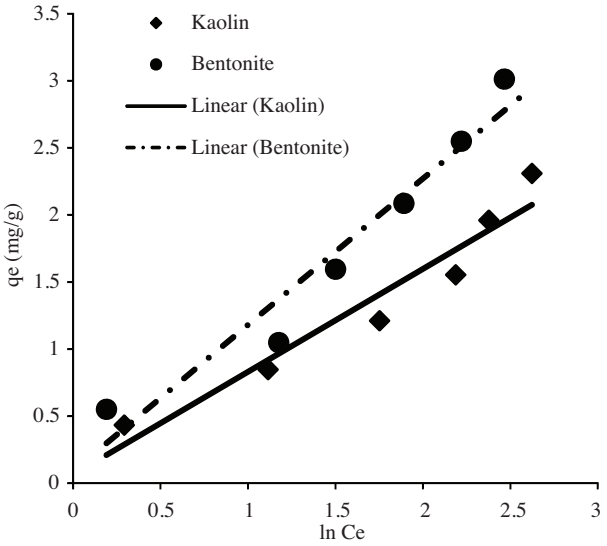

Figure 8. Temkin isotherm (formaldehyde concentration: 30-80 mg/L; agitation speed: 125 rpm; temperature: 303 K; dose: 1.0 g/25 mL for kaolin and 0.8 g/25 mL for bentonite).

Conclusion

Detailed analysis of the experimental data was carried out using adsorption isotherms to explain the adsorption of formaldehyde on kaolin and bentonite clays. Bentonite shows a greater tendency to adsorb formaldehyde as compared to kaolin. Maximum adsorption capacity of kaolin and bentonite indicates that 1 g of kaolin can adsorb 3.41 mg of formaldehyde while in the case of bentonite it is 5.03 mg of formaldehyde per gram. The present study indicated that instead of chemicals and other expensive treatments, non-hazardous clays like bentonite and kaolin can be used as formaldehyde removers from wastewaters and industrial effluents to overcome water pollution.

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