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Sorption/desorption studies on some natural minerals for the removal of toxic organic pollutants from aqueous solution

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ABSTRACT

This work explored the sorption potential of Kyanite and Pyrolusite for the removal of phenol, chlorophenol (CP) and β -Naphthol (BN). Uptake of phenol and CP was negligible on Kyanite and Pyrolusite. BN was significantly sorbed on these two sorbents. Maximum uptakes of BN on Kyanite and Pyrolusite were observed in acidic medium. Langmuir and Freundlich isotherms confirm favorable sorption of BN on Kyanite and Pyrolusite with high sorption efficiency in acidic medium. The kinetics studies indicate that Pseudo-second-order models are better obeyed than Pseudo-first-order model. The intraparticle diffusion models show the lines were not passing through the origin. Statistical data analysis also verifies the applicability of Pseudo-second-order model. Desorption studies were carried out by a batch process. 100% BN was recovered from Pyrolusite when hexane and hexane:propanol mixture (99:1) was used as eluent.

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1. Introduction

Deterioration in soil, surface and ground water quality due to existence of organic pollutants promotes the research, targeting environmental protection in many ways. Various toxic organic chemicals are potentially hazardous to human health and also to the terrestrial and aquatic ecosystem, are being discharged into the environment as a result of industrial, agricultural and domestic activities [1].

Aromatic pollutants particularly phenols and its derivatives are very toxic, many are known or suspected to be human carcinogens [2–4]. Phenolic compounds are water soluble and highly mobile and hence are likely to reach drinking water sources downstream from discharges, where, even at low concentrations, they can cause severe odour and taste problems and pose risks to populations [1]. Ingestion of phenols in concentrations from 10 to 240 mg/L for long periods causes mouth irritation, diarrhea, excretion of dark urine and vision problems [5]. The lethal phenol concentration in blood ranges approximately from 4.7 to 130 mg/L [6]. Phenolic compounds are present in waste effluents discharged from paint, solvent, petroleum, petrochemical, pharmaceutical, plastic, pesticide, iron and steel, paper and pulp industries. Large scale gasification and carbonization plants generate huge quantities of high

strength phenolic wastewater [7]. A number of methods such as ozonation [8], photo-Fenton degradation [9], catalytic wet oxidation [10], oxidation [11], electrochemical treatment [12], biological methods [13,14], reverse osmosis [15], pervaporation [16] and sorption [17–19], have been used for removal of organic pollutants. Despite the availability of the above mentioned processes for the removal of organic pollutants, the sorption process still remains the best as it can generally remove all types of organic pollutants, and the effluent treatment is convenient because of a simple design and easy operations. In particular, sorption on commercially available activated carbon is one of the most popular methods for the removal of pollutants from wastewater [20] as it possesses high sorption efficiency owing to its high surface area and well defined microporous structure, but, the drawback of using commercially available activated carbon is its economic viability. Synthetic sorbents are also relatively expensive hence use of natural sorbents is an active area of research. The sorption properties of various natural/non-conventional sorbents like peat [21], activated sludge [22], chitosan [23], or cyclodextrin derivatives [24] were explored by various authors for the removal of various organic pollutants. The advantage of using natural sorbents over activated carbon is that the sorbed solute can be extracted (or preconcentrated) with some suitable eluent. This preconcentration process may help in the identification and determination of traces of organic pollutants present in wastewater.

Kyanite and Pyrolusite are easily available minerals in India. Pyrolusite (a manganese ore) is abundantly available in Kalahandi, Orissa. It is steel gray to a solid black in earthy specimens. It is

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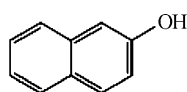
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metallic to dull in weathered or thinly crusted specimens. The crystals are opaque, translucent in only thin splinters. It has a tetragonal geometry. The crystals of Pyrolusite are typically massive and compact forms, but also fibrous, acicular, columnar, concretionary, scaly and earthy forms are well known. A thin dendritic habit is commonly seen encrusted on sandstones and siltstones and will form wonderful fern or tree like patterns that are often mistaken for fossil plants. A variety with large, easily visible crystals is called polianite, and occurs as minute prismatic crystals with a square or rectangular cross-section and wedge-shaped terminations [25].

Kyanite is a triclinic crystalline mineral like other aluminosilicates and closely approximates Al_2SiO_5 . The color is ranging from colorless to blue. Kyanite, when calcined, is used in refractory products and it is the most important of the aluminosilicates [26]. Kyanite is a common constituent of the Archaean rocks of India and abundantly available in Singbhum district of Bihar, Himalayas, Andhra Pradesh and Tamil Nadu. The occurrence of Kyanites invariably in crystalline schistose rocks indicate that it is a product of metamorphism of alumina-bearing sediments most clayey materials, which have been metamorphosed under enormous pressure at a great depth in the earth's crust. It occurs extensively in commercial quantities and is used as a refractory material. It is also used in metallurgical, glass and ceramics and cement industries. Kyanite refractories are generally used in furnaces for smelting non-ferrous metals like copper, zinc and nickel alloys [27].

In this paper we have tried to explore the sorption behavior of phenol, chlorophenol (CP) and β -Naphthol (BN) onto Kyanite and Pyrolusite. There are some commercially available adsorbents like activated carbon but recovery of organic compounds from these adsorbents is very poor. The adsorbents we have studied shows excellent recovery of BN as compared to commercially available activated carbon showing the economic importance of these studied adsorbents.

BN, an isomeric form of Naphthol, $\text{C}_{10}\text{H}_7\text{OH}$, occurs as white crystals and used in making antioxidants, pigments, and dyes [28]. It is also used in rubber as an antioxidant. The structure of BN is given below. The solubility of BN in water is 8.18 mol/m^3 . The dissociation constant (pK_a) for BN is 9.5. Kinetics studies for the sorption of BN on Kyanite and Pyrolusite were done in acidic medium at different concentrations. Isotherm studies were done in acidic medium and compared with neutral medium. Desorption studies were done in acidic medium and compared with activated carbon.



Structure of BN

2. Materials and methods

2.1. Sorbents

Kyanite and Pyrolusite were used as sorbents. The sorbents were crushed and sieved to a 300–100 μm particle size, washed several times with Double Distilled Water (DDW) in order to remove dirt and finally dried in an oven at 60°C for 24 h.

2.2. Reagents and samples

Stock solution of CP, Phenol and BN (1000 mg/L) (Analytical Reagent Grade) were prepared in methanol (HPLC grade). All other reagents and solvents used were of HPLC grade.

2.3. Apparatus

The samples were analyzed by High performance liquid chromatography (HPLC) equipped with Shimadzu spectrophotometric detector model SPD 6AV, pump LC 6A and system controller SCL 6B. Peak area and retention time was calculated with Shimadzu chromatopack C-R6A data processor (Shimadzu Scientific Instrument Inc. Japan).

The samples and reagents used were filtered and degassed in an ultrasonic shaker (Elma, Germany) for 10 min.

2.4. Sample analysis

The analysis of samples was carried out on $0.6\Phi \times 15 \text{ cm}$ shim-pack CLC ODS (Shimadzu, Japan) column at ambient temperature. Using methyl alcohol (HPLC grade) and 0.1 M NaClO_4 mixture (80:20) as mobile phase with flow rate of 0.5 mL min^{-1} . The effluents were monitored at 270 nm (Phenol), 274 nm (CP) and 256 nm (BN) by Ultra Violet (UV) Detector at 0.16 AUFS.

2.5. Sorption studies

Sorption studies were carried out by batch process. 0.5 g of sorbent with 50 mL of sorbate of desired concentration and pH was shaken in a temperature controlled shaker incubator at 180 rpm till equilibrium was reached (24 h). The mixture was then filtered using Whatman No. 41 filter paper and final concentration of sorbate in the filtrate was determined by RP-HPLC.

The % sorption of sorbate and equilibrium sorption capacity (q_e), were calculated using the following relationships:

$$\text{sorption (\%)} = \left[\frac{C_o - C_e}{C_o} \right] \times 100 \quad (1)$$

$$\text{sorption capacity } (q_e) (\text{mg/g}) = [C_o - C_e] \times \frac{V}{W} \quad (2)$$

where C_o is the initial concentration of sorbate (mg/L); C_e is the equilibrium sorbate concentration (mg/L); V is the volume of the solution (L); W is the mass of the sorbent (g).

2.6. Desorption studies

Batch process was used for desorption. 0.5 g of sorbent with 50 mL sorbate of desired concentration was shaken in shaker incubator at 180 rpm till equilibrium was established. The unadsorbed sorbate in the filtrate was determined by RP-HPLC. The sorbent was washed several times with DDW. It was then transferred to another stoppered cork flask and was treated with 50 mL solvent for 24 h in shaker at 180 rpm speed. The desorbed matter was then determined by RP-HPLC.

3. Results and discussion

Sorption of Phenol, CP and BN (initial concentration 50 mg/L) on Pyrolusite and Kyanite is given in Table 1. Phenol and CP were not sorbed on Kyanite and Pyrolusite. BN was sorbed to some extent.

Table 1
Sorption of some organic pollutants on Kyanite and Pyrolusite.

| S. no. | Organic pollutants | Sorption (%) | |
|--------|--------------------|--------------|------------|
| | | Kyanite | Pyrolusite |
| 1 | CP | 0 | 0 |
| 2 | Phenol | 0 | 0 |
| 3 | BN | 24 | 62 |

Conditions: Initial conc. 50 mg/L; contact time 24 h; pH 7.1; temperature $298 \pm 2 \text{ K}$; agitation speed 180 rpm.

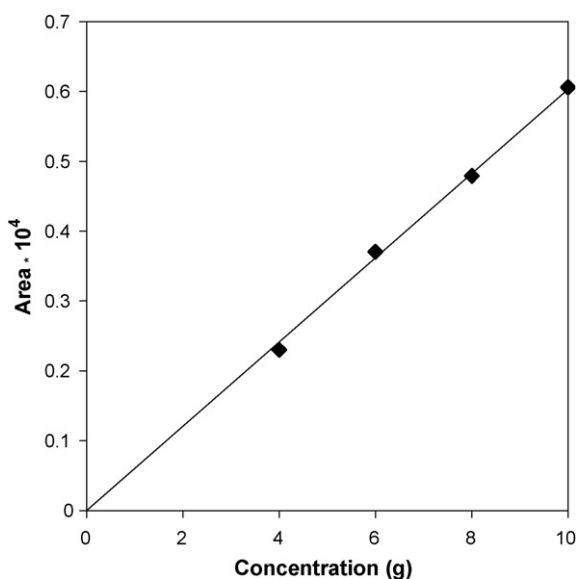


Fig. 1. Calibration plot for BN.

The sorption of BN on Pyrolusite was more as compared to Kyanite. Therefore BN was chosen for detailed study.

3.1. Determination of Organic compounds by RP-HPLC

Phenol, CP and BN are eluted when a mixture of methyl alcohol and 0.1 M NaClO₄ (80:20) is passed through ODS column. The peaks are sharp without any tailing. The retention time of BN is 7.968. Calibration curve of BN is shown in Fig. 1. The calibration curve of BN (Fig. 1) indicates that a minimum of 4 µg of BN can be determined accurately by RP-HPLC.

3.2. Effect of pH

The effect of solution pH on the sorption of BN onto Kyanite and Pyrolusite is shown in Fig. 2. The sorption of BN onto Kyanite and Pyrolusite was maximum at pH 3 and 4 respectively. The sorption of BN onto Kyanite and Pyrolusite decreases with further increase in pH. This may be due to the amphoteric nature of these natural minerals. The sorption of weak electrolytes on the surface of porous

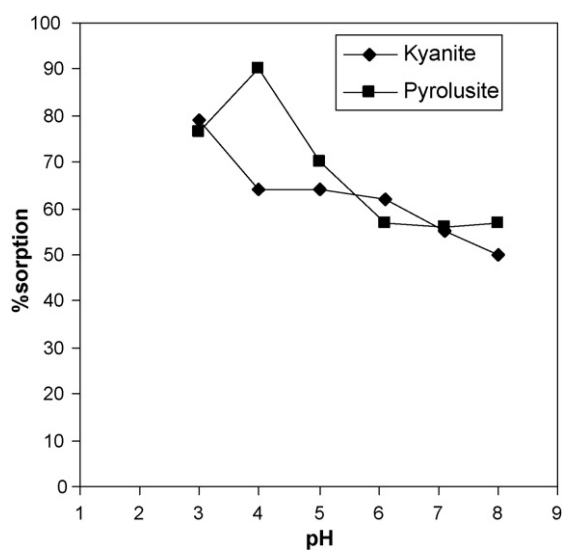


Fig. 2. Effect of pH on the sorption of BN on Kyanite and Pyrolusite.

amphoteric sorbents from aqueous solutions depends, among other things, on two important factors. One of them is the degree of dissociation of the electrolyte and the other is the dominant charge on the surface of the solid. Both factors are dependent on the pH of the aqueous solution [29]. When pH was increased, the surfaces of the sorbent start acquiring negative charge and at the same time BN starts dissociating thus naphtholate ions generated at higher pH were repelled by negative charge on the sorbent surface. This results a decrease in the sorption of BN with increase in pH.

3.3. Effect of contact time and initial concentration

Sorption studies of BN onto Kyanite and Pyrolusite at various initial concentrations were carried at different time intervals (0–420 min) at pH 3 and 4 respectively. The maximum equilibrium uptake (q_e) onto Kyanite was found to be 27.6, 41, 44.4 and 79.8 mg/g at 40, 50, 60 and 100 mg/L initial BN concentrations (Fig. 3a). The maximum equilibrium uptake (q_e) onto Pyrolusite was found to be 2.38, 3.92, 4.21 and 8.75 mg/g at 40, 50, 60 and 100 mg/L initial BN concentrations (Fig. 3b). The increase of initial concentration increases the sorption capacity of BN on both Kyanite and Pyrolusite. Initially, the sorption was rapid and then slows down attaining an equilibrium point. The equilibrium attained easily when the initial concentration was low, because initially available sites on the surface of sorbent (means the surface is unsaturated) is

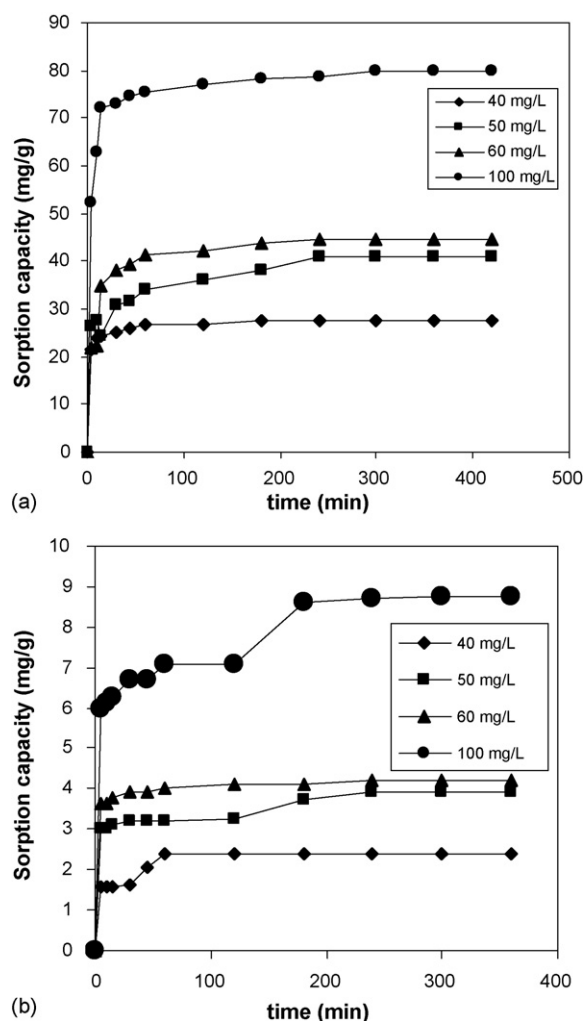


Fig. 3. (a) Effect of contact time on the sorption of BN on Kyanite at pH 3; (b) effect of contact time on the sorption of BN on Pyrolusite at pH 4.

Table 2a
Kinetics parameters for the sorption of BN on Kyanite.

| Conc. (mg/L) | $q_{e(\text{exp})}$ (mg/g) | Pseudo-first-order | | | Pseudo-second-order | | | Intraparticle diffusion model | | |
|--------------|----------------------------|-----------------------------|-------|--------|-----------------------------|-------|--------|-------------------------------|-------|--------|
| | | $q_{e(\text{theo})}$ (mg/g) | K_1 | r^2 | $q_{e(\text{theo})}$ (mg/g) | K_2 | r^2 | $q_{e(\text{theo})}$ (mg/g) | K_d | r^2 |
| 40 | 27.6 | 5.9 | 0.031 | 0.9541 | 27.8 | 0.015 | 0.9998 | 22.24 | 0.453 | 0.8069 |
| 50 | 41 | 14.8 | 0.009 | 0.9487 | 38.7 | 0.004 | 0.9977 | 24.66 | 1.048 | 0.9835 |
| 60 | 44.4 | 9.5 | 0.014 | 0.9571 | 45.4 | 0.003 | 0.9995 | 33.99 | 0.727 | 0.8839 |
| 100 | 79.8 | 7.9 | 0.008 | 0.9804 | 78.1 | 0.006 | 0.9996 | 70.56 | 0.546 | 0.9770 |

Conditions: pH 3; temperature 298 ± 2 K; agitation speed 180 rpm.

large to the sorption and as the contact time increases it gradually decreases until it attains equilibrium [30]. Sorption capacity of BN on Kyanite was higher in comparison to Pyrolusite.

3.4. Kinetics of sorption

The main objective of the Kinetic studies is to determine equilibrium contact time. Various kinetics models including the Pseudo-first-order kinetics, Pseudo-second-order kinetics and intraparticle diffusion models have been applied to the experimental data to predict the sorption kinetics.

The Pseudo-first-order rate equation can be written as follows [31]:

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

where q_e and q_t are the amounts of sorbate sorbed per unit weight of sorbent (mg/g) at equilibrium and at time t respectively; K_1 is the rate constant of Pseudo-first-order reaction (1/min); t is the contact time (min).

The Pseudo-second-order kinetics model is expressed as follows [31]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \times t \quad (4)$$

where q_e and q_t are the amounts of sorbate sorbed per unit weight of sorbent (mg/g) at equilibrium and at time t respectively; K_2 is the rate constant of Pseudo-second-order reaction (g/mg-min); t is the contact time for sorption (min).

Intraparticle diffusion model based on the theory proposed by Weber and Morris [32] was tested to identify the diffusion mechanism. This model is expressed as

$$q_t = K_d t^{1/2} \quad (5)$$

where K_d (mg/g-min^{1/2}) is the intraparticle diffusion rate constant.

The data shows that the values of correlation coefficient (r^2) for Pseudo-first-order kinetics model (Figure not shown) and intraparticle diffusion model were lower as compared to Pseudo-second-order kinetics model at different initial concentration values for both Kyanite and Pyrolusite (Fig. 4a–d) (Tables 2a and 2b). The values of $q_{e(\text{theo})}$ were very close to $q_{e(\text{exp})}$ values for Pseudo-second-order kinetics model at different concentration values showing that Pseudo-second-order kinetics model for the sorption of BN onto Kyanite and Pyrolusite best describes the sorption process.

Table 2b
Kinetics parameters for the sorption of BN on Pyrolusite.

| Conc. (mg/L) | $q_{e(\text{exp})}$ (mg/g) | Pseudo-first-order | | | Pseudo-second-order | | | Intraparticle diffusion model | | |
|--------------|----------------------------|-----------------------------|-------|--------|-----------------------------|-------|--------|-------------------------------|-------|--------|
| | | $q_{e(\text{theo})}$ (mg/g) | K_1 | r^2 | $q_{e(\text{theo})}$ (mg/g) | K_2 | r^2 | $q_{e(\text{theo})}$ (mg/g) | K_d | r^2 |
| 40 | 2.38 | 1.04 | 0.027 | 0.9609 | 2.6 | 0.533 | 0.9814 | 1.108 | 0.153 | 0.9764 |
| 50 | 3.92 | 1.02 | 0.009 | 0.9642 | 3.9 | 0.035 | 0.9917 | 2.794 | 0.070 | 0.9049 |
| 60 | 4.21 | 0.6 | 0.019 | 0.9450 | 4.14 | 0.160 | 0.9999 | 3.612 | 0.041 | 0.9644 |
| 100 | 8.75 | 3.55 | 0.017 | 0.9886 | 8.94 | 0.011 | 0.9938 | 5.509 | 0.203 | 0.9375 |

Conditions: pH 4; temperature 298 ± 2 K; agitation speed 180 rpm.

For intraparticle diffusion, correlation coefficient (r^2) value for the sorption of BN on Kyanite and Pyrolusite were lower than the values for Pseudo-second-order kinetics values. The intraparticle diffusion plots (Fig. 4c and d) show that the lines were not passing through the origin. This deviation from the origin might be due to the difference in the mass transfer rate in the initial and final stages of sorption of BN on Kyanite and Pyrolusite [33].

Kinetics models were verified statistically by the sum of squared errors (SSE, %) given by [34]

$$\text{SSE (\%)} = \frac{\sqrt{\sum (q_{e(\text{exp})} - q_{e(\text{theo})})^2}}{N} \quad (6)$$

where N is the number of data points. The SSE values for Kyanite for the Pseudo-first-order, Pseudo-second-order and intraparticle diffusion models were 43.45%, 1.52% and 11.05%, respectively and for Pyrolusite the SSE values for the Pseudo-first-order, Pseudo-second-order and intraparticle diffusion models were 3.59%, 0.15% and 1.85%, respectively. Lower the value of SSE% the better is the fit. It was found that the Pseudo-second-order model yielded the lowest SSE value for both sorbents. This statistical analysis data test also proves that the sorption of BN on Kyanite and Pyrolusite could be best described by the Pseudo-second-order kinetics model which is based on the equilibrium chemical adsorption that predicts the behavior over the whole range of studies, strongly supporting the validity and agrees with chemisorption being rate-controlling [35].

3.5. Sorption isotherms

Sorption isotherm is basically important to describe how solutes interact with sorbents, and is critical in optimizing the use of sorbents [33]. The equilibrium of a solute separated between the liquid and solid phases is described by Langmuir and Freundlich models. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of sorption sites of uniform strategies of sorption with no transmigration of sorbate in the plane of surface [36]. The Freundlich isotherm, on the other hand, assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage [36]. These two models were used to analyze the sorption data for the sorption of BN on Kyanite and Pyrolusite in both acidic and neutral medium. Langmuir model may be defined as

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{1}{q_m} \times C_e \quad (7)$$

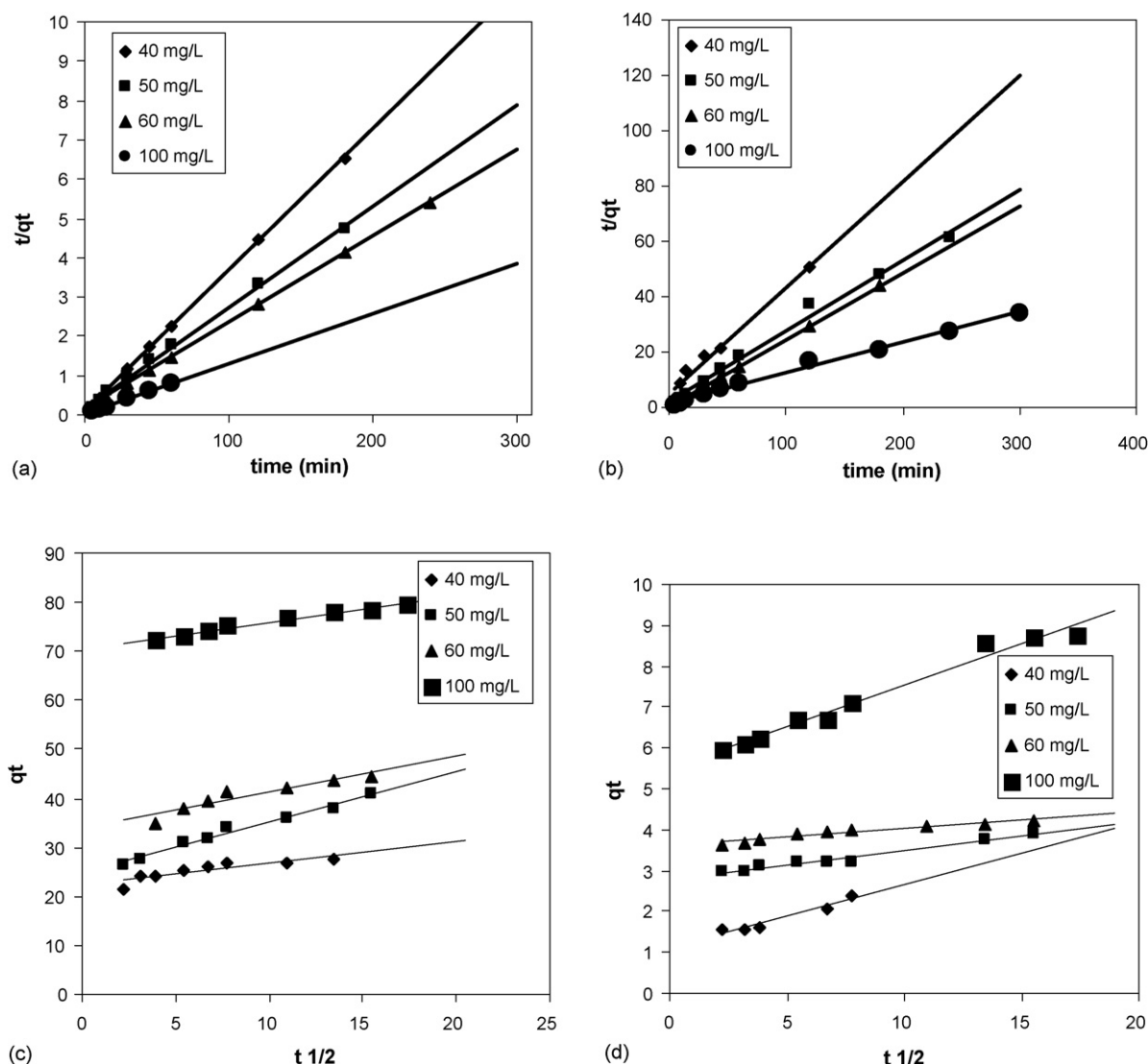


Fig. 4. (a) Pseudo-second-order kinetics for the sorption of BN on Kyanite; (b) Pseudo-second-order kinetics for the sorption of BN on Pyrolusite; (c) Intraparticle diffusion plot for the sorption of BN on Kyanite; (d) Intraparticle diffusion plot for the sorption of BN on Pyrolusite.

Table 3a

Isotherms parameters for the sorption of BN on Kyanite.

| pH | $q_m(\text{exp})$ (mg/g) | Langmuir isotherm | | | | Freundlich isotherm | | |
|-----|--------------------------|--------------------------|------------|-------|-------|---------------------|-------|-------|
| | | $q_m(\text{cal})$ (mg/g) | b (L/mg) | R_L | r^2 | $\log K_f$ | $1/n$ | r^2 |
| 7.1 | 1.31 | 1.31 | 0.277 | 0.035 | 0.993 | 0.1465 | 0.017 | 0.054 |
| 3.0 | 5.86 | 6.94 | 0.128 | 0.072 | 0.999 | 0.2638 | 0.429 | 0.952 |

Conditions: Temperature 298 ± 2 K; agitation speed 180 rpm; contact time 24 h.

where q_e is the amount of BN sorbed per unit weight of sorbent (mg/g); C_e is the equilibrium concentration of BN (mg/L); b is the coefficient related to the affinity between the sorbent and sorbate (L/mg); q_m is the maximum sorption capacity determined by the number of reactive surface sites in an ideal monolayer system (mg/g).

Table 3b

Isotherms parameters for the sorption of BN on Pyrolusite.

| pH | $q_m(\text{exp})$ (mg/g) | Langmuir isotherm | | | | Freundlich isotherm | | |
|-----|--------------------------|--------------------------|------------|-------|-------|---------------------|-------|-------|
| | | $q_m(\text{cal})$ (mg/g) | b (L/mg) | R_L | r^2 | $\log K_f$ | $1/n$ | r^2 |
| 7.1 | 2.6 | 82.64 | 0.007 | 0.588 | 0.727 | 0.1808 | 0.181 | 0.903 |
| 4.0 | 6.1 | 5.07 | 0.783 | 0.013 | 0.994 | 1.1279 | 0.156 | 0.813 |

Conditions: Temperature 298 ± 2 K; agitation speed 180 rpm; contact time 24 h.

Results show that for Langmuir model, the values of $q_m(\text{cal})$ are very near to $q_m(\text{exp})$ for the sorption of BN onto Kyanite at pH 7.1 and 3 (Table 3a). On the other hand for Pyrolusite at pH 4 the values of $q_m(\text{exp})$ are nearer to $q_m(\text{cal})$ (Table 3b). The correlation coefficient (r^2) values obtained for Kyanite at pH 7.1 and 3 and for Pyrolusite at pH 4 (Fig. 5a and b) are nearer to 1 favoring Langmuir isotherm.

Table 4
Removal/recovery of BN from Activated Carbon (AC), Kyanite and Pyrolusite by batch process.

| Solvent | Amount of BN loaded (mg) | Activated carbon | | Pyrolusite | | Kyanite | |
|------------------------|--------------------------|--------------------|-----------------------|--------------------|-----------------------|--------------------|-----------------------|
| | | Amount sorbed (mg) | Amount recovered (mg) | Amount sorbed (mg) | Amount recovered (mg) | Amount sorbed (mg) | Amount recovered (mg) |
| Hexane | 2.5 | 2.5 | 0.00 | 1.87 | 1.87 | 1.85 | 0.00 |
| Hexane | 0.25 | – | – | 0.2075 | 0.14 | – | – |
| Hexane:propanol (99:1) | 2.5 | 2.5 | 0.00 | 1.87 | 1.86 | 1.85 | 0.225 |
| Butanol | 2.5 | 2.5 | 0.00 | 1.92 | 0.00 | 1.86 | 0.66 |
| Acetonitrile | 2.5 | 2.5 | 0.00 | 1.87 | 0.45 | 1.82 | 0.00 |
| Water | 2.5 | 2.5 | 0.00 | 1.87 | 0.00 | 1.85 | 0.00 |
| Propanol | 2.5 | 2.5 | 0.00 | 1.87 | 0.00 | 1.87 | 0.00 |
| 0.05 M NaOH | 2.5 | 2.5 | 0.00 | 1.87 | 0.00 | 1.85 | 0.00 |
| 0.1 M HCl | 2.5 | 2.5 | 0.00 | 1.87 | 0.00 | 1.85 | 0.00 |
| Isobutylmethyl ketone | 2.5 | 2.5 | 0.00 | 1.88 | 0.00 | 1.86 | 0.00 |

Conditions: Temperature 298 ± 2 K; pH 3–4; amount of sorbent 0.5 g; amount of solution 50 mL; contact time 24 h; agitation speed 180 rpm.

The essential feature of Langmuir model can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (R_L) given by relation [33]:

$$R_L = \frac{1}{1 + bC_0} \quad (8)$$

where C_0 is the highest initial concentration.

If $0 < R_L < 1$ favorable sorption, $R_L > 1$ unfavorable sorption, $R_L = 1$ linear sorption, $R_L = 0$ irreversible sorption. The values of R_L for the sorption BN onto Kyanite and Pyrolusite are well in the range $0 < R_L < 1$ showing favorable sorption of BN (Tables 3a and 3b).

Freundlich sorption model is given as

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (9)$$

where C_e is the equilibrium concentration (mg/L); q_e is the amount of BN sorbed per unit weight of sorbent (mg/g), K_f is the sorption capacity of sorbent; $1/n$ is the empirical constant related to the efficiency of the sorption, if $1/n > 1$ the sorption is low while if $1/n < 1$ the sorption is good.

Tables 3a and 3b (Figures not given) show the values of K_f on Kyanite and Pyrolusite were higher in acidic medium indicating the higher sorption efficiency in acidic medium. The values of $1/n$ were well below 1. However, Freundlich isotherms are not well obeyed by Kyanite at pH 3 and 7.1 as indicated by r^2 values (Table 3a). In case of Pyrolusite Freundlich isotherm is not well obeyed at pH 4 and 7.1 as indicated by r^2 values (Table 3b). It can be concluded that Langmuir isotherm is best fit for Kyanite at pH 3 and 7.1. While Langmuir isotherm is best obeyed by Pyrolusite at pH 4.0.

3.6. Desorption studies

Desorption of BN on Kyanite, Pyrolusite and activated carbon using different solvents is summarized in Table 4. There is no recovery of BN from activated carbon illustrating that it cannot be regenerated under normal conditions. The recovery of BN from Kyanite 35% with butanol and 13.8% with hexane:propanol mixture (99:1). This behavior shows that BN is very strongly sorbed on Kyanite and cannot be recovered completely by any of these solvents. The recovery of BN from Pyrolusite is 24.1% when acetonitrile is used as an eluent. Recovery is 100% and 67.5% with hexane when 2.5 and 0.25 g of BN was loaded respectively. With hexane:propanol mixture (99:1) the recovery of BN from Pyrolusite is 100%.

4. Conclusions

1. Sorption of phenol, chlorophenol on Kyanite and Pyrolusite is negligible but the sorption of BN on Kyanite and Pyrolusite is pH and concentration dependent.
2. Isotherms suggest higher sorption efficiency in acidic medium. Sorption of BN onto Kyanite follows Langmuir model in both acidic and neutral medium. The sorption of BN onto Pyrolusite obey Langmuir model in acidic medium. Separation factors (R_L) indicate that sorption of BN on Kyanite and Pyrolusite is favorable process.

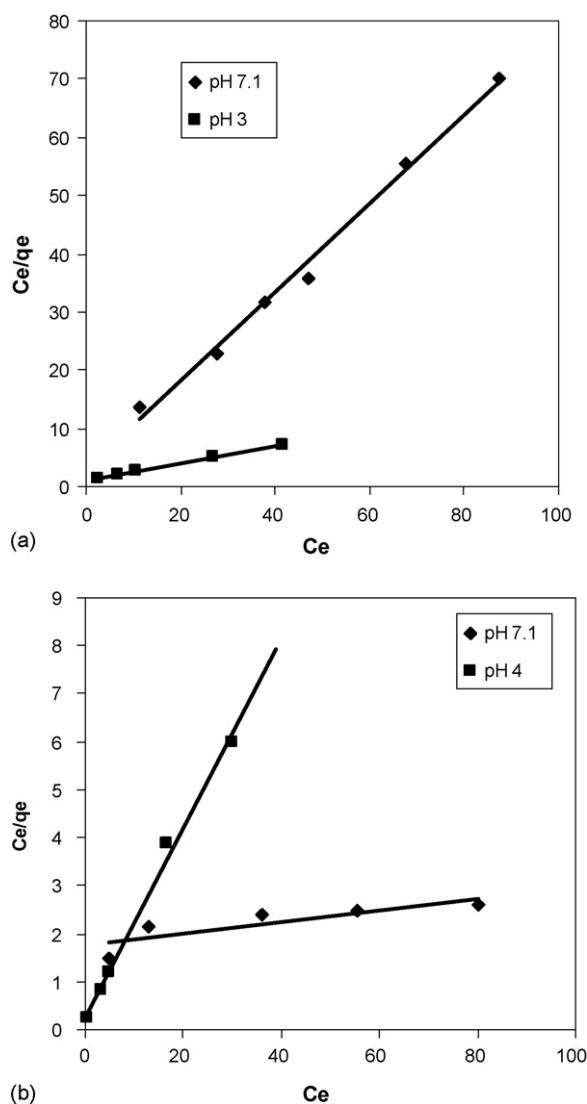


Fig. 5. (a) Langmuir plot for the sorption of BN on Kyanite; (b) Langmuir plot for the sorption of BN on Pyrolusite.

3. Kinetics and statistical data show better applicability of Pseudo-second-order kinetics model for the sorption of BN onto Kyanite and Pyrolusite.
4. The recovery of BN is negligible from activated carbon while recovery of BN is 100% from Pyrolusite when hexane and mixture of hexane:propanol (99:1) are used as solvents. This behavior of Pyrolusite may be utilized for the removal and preconcentration of BN from water and wastewater.

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