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Oil-Rich Sludge Based Adsorbents for Rhodamine B Removal

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Abstract: This study was aimed at evaluating the possible use of oil-rich sludge as adsorbents for dye removal. The sludge-adsorbents were prepared through treatment using HCl and KOH andwere then characterized according to BET surface area and surface functional groups. Rhodamine B was selected as model dye andbatch equilibrium adsorption of dyewas performed with the treated and untreated adsorbents. The result shows that the BET surface area for KOH-treated adsorbent is the highest (2.08 m^2 g^{-1}) compared to the other two samples. The equilibrium adsorption capacity was well correlated with the specific surface area of adsorbents. Also, the Langmuir model was well-fitted to the adsorption data, suggesting that the adsorption is monolayer in nature and is possibly of a chemical-type. With suitable treatment, oil-rich sludge could be a promising adsorbent for dye removal from water.

Key words: Adsorbent, adsorption, chemical treatment, oil-rich sludge, rhodamine B

INTRODUCTION

Synthetic dyes are more preferred to be applied on fabrics because they are cheaper, brighter and more color-fast. However, the chemicals used in producing synthetic dyes are often carcinogenic and highly toxic andmay cause detrimental consequences to the aquatic environment and human health. It is estimated that over 700 thousand tons of synthetic dyes are produced annually worldwide. Textile industry that requires large amount of dyes for its products has been identified as one of the largest polluters of water. Nearly 200 thousand tons of dyes are lost to the effluent every year during the dyeing and finishing operations due to the lack of efficiency (Chequer *et al*., 2013). Dyes may remain in the environment for a longer period due their high stability to light, temperature and chemicals. Dyes are hard to be removed by natural occurrences because they are designed to resist biodegradation. Dyes are also capable to decrease light penetration and photosynthetic activity, leading to oxygen deficiency and deaths of fish species and aquatic plants. This can also limits the downstream beneficial usage such as irrigation and drinking water.

Other than dyes, sludge is also of considerable concern to the environmentalists.Sewage sludge is an inevitable solid byproduct of wastewater treatment andits amount has increased rapidly due to urbanization and industrial development (Li *et al*., 2011). For example, China's municipal wastewater treatment plants collected almost 5.3 million tons of dried sludge annually and it is expected to increase by 10% every year (Fang *et al*., 2010). Sewage sludge is mostly consists of offensive, pathogenic and toxic substances (Li *et al*., 2011). Sludge also produces bad odors and is a source of water and ground pollution.Therefore, it is important to search for cost effective and sustainable methods of sludge handling and disposal.

Various methods have been used to dispose sludge such as incineration, land filling, land application, road surfacing, compression into building blocks and conversion to fertilizer. Incineration and land filling are common methods for sludge disposal but they are expensive and may lead to secondary pollutions (Zaini *et al*., 2013). Other factors such as legislative and environmental constraints, reducing the availability of land andcost effective and renewable disposal possibilities must also be taken into consideration.The most effective method available for removing dyes from effluent is adsorption by activated carbon (Zaini *et al*., 2013; Geethakarthi and Phanikumar, 2010). However, the commercial activated carbon is expensive due to limited source of precursor. This has triggered search for cheap

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and abundant source of adsorbent (Xu *et al*., 2015). A promising candidate under this category is oil-rich sludge.

Therefore, this study was carried out to evaluate the possible use oil-rich sludge as adsorbents for colour removal from water. Batch adsorption was performed and the adsorptive data were fitted to the isotherm models. The results are expected to shed some light for ‘use waste to treat other waste’ approach.

MATERIALS AND METHODS

Oil-rich sludge was supplied by IFFCO (Malaysia). The sludge is in wet condition at room temperature andwas dried in oven to remove moisture. The moisture content was recorded as 60.2%. The dried sludge contains 61.8% carbon, 9.7% hydrogen, 0.3% nitrogen, 0.1% sulphur and 28.1% oxygen (by difference). It is assumed that the sludge is mainly consists of organic materials which are suitable for adsorbent with good adsorption properties. All chemicals used are of analytical reagent grade.

Preparation and characterization of adsorbents: The dried sample was cleaned manually by segregating any alien matter. It was ground and sieved to a particle size of about 3 mm. Then it was dried in furnace at 300°C for 2 h to remove excess oil. This sample was designated as untreated sludge. The sludge sample was immersed in 5 M HCl solution for 24 h at room temperature.After that, the sample was washed repeatedly with distilled water until the pH is constant. Washing with distilled water can decrease the ash content of adsorbent and improve the specific (BET) surface area and porosity. The treated sludge sample was then dried at 110°C for 24 h. This sample was designated as HCl-treated sludge. The purpose of this treatment is to remove impurities that block the pores and progressively eliminate cations or minerals on the surface.Acid treatment is usually used to change the hydrophilic or hydrophobic properties of adsorbent for adsorption of various ions or organics.

The sludge sample was immersed in 5 M KOH solution and was dried in oven at 100°C overnight. Then, the impregnated sample was heated in furnace at 600°C for 2 h. The resultant adsorbent was washed repeatedly with distilled water until the pH is constant anddried at 110°C for 24 h. This sample was designated as KOH-treated sludge. KOH is also able to solidify the carbon network andcan increase specific surface area and micro porosity of adsorbent due to dissolution of amorphous material. The specific (BET) surface area was determined using a Micrometics PulseChemisorp 2705 analyzer by N_2 adsorption-desorption isotherm at 77 K. The samples were first outgassed at 300°C for 2 h before analysis. The surface area was calculated with an assumption that the surface area occupied by a physisorbed nitrogen molecule is 162 nm^2. The FTIR analysis was performed on a IRTracer-100 Shimadzu instrument. The FTIR spectra is essential to determine the functional groups.A small amount of sample was placed on sample holder andwas scanned from 450-4000 cm^{-1}.

Adsorption of rhodamine B: Rhodamine B of commercial purity was used without further purification. About 0.5 g of rhodamine B was weighed using analytical balance and then dissolved with distilled water in 1 L volumetric flask to prepare stock solution of 500 ppm. Necessary dilutions were needed to obtain varying concentrations of rhodamine B solution.

About 0.05 g of adsorbent was brought into intimate contact with 50 mL rhodamine B solution of varying concentrations. The mixtures were allowed to equilibrate on orbital shaker at 120 rpm and room temperature for 72 h. The residual concentration was measured using visible spectrophotometer (Halo Vis-10, Dynamica) at a wavelength of 555 nm. The adsorption capacity (mg/g) was calculated by simple material balance andthe data were analyzed by widely used isotherm models, namely Langmuir, Freundlich and Redlich-Peterson (Zaini *et al*., 2013).

RESULTS AND DISCUSSION

Characteristics of adsorbents: Table 1 shows the characteristics of sludge adsorbents. The yield for adsorbent with no treatment (after being heated at 300°C in furnace) is higher than the adsorbents that receive treatment. Adsorbent that receive HCl treatment gives lower yield as unnecessary element such as ash that might interrupt the porosity is removed while some volatiles are liberated when the KOH-treated sludge was heated at 600°C in furnace. The untreated sludge has a pH of 6.65 which is slightly acidic. The adsorbent that was treated with HCl becomes more acidic while KOH-treated sludge is slightly basic. The untreated oil-rich sludge has a specific surface area of 0.45 m^2 g^{-1}. Upon the chemical treatment, the specific surface area increased to 1.05 and 2.08 m^2 g^{-1} for HCl-treated and KOH-treated sludge adsorbents, respectively. It is also predicted that KOH

Table 1: Characteristics of oil-rich sludge based adsorbents

Adsorbent	Yield (%)	pH	Specific surface area (m^2 g^{-1})
Untreated	86.1	6.7	0.45
HCl-treated	71.2	4.6	1.05
KOH-treated	53.9	8.9	2.08

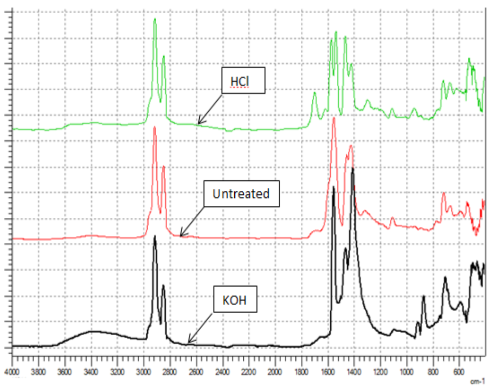

Fig. 1: FT-IR spectra for untreated sludge, HCl-treated and KOH-treated adsorbents

treated sludge would offer a higher adsorption performance due to a higher specific surface area. A higher surface area may indicate greater interaction probabilities between the adsorbate molecules and the adsorbent sites.

Figure 1 displays the FTIR profiles of adsorbents. The spectra were obtained in the form of absorption transmittance on different frequency ranges. The surface functional groups available on the adsorbent surface were determined from peaks shown in the spectra. From Fig. 1, the three adsorbents possess similar surface groups of saturated aliphatic (alkane) methylene C-H asymmetric and symmetric stretch for peaks ranging from 2915-2935 cm^{-1} and 2845-2865 cm^{-1}, respectively. Also, C-H asymmetric bend at wave number of 1430-1470 cm^{-1}. Besides, there is another small band between 1490 and 1600 cm^{-1} which can be assigned to C=C aromatic ring. A broad peak centred at 3400 cm^{-1} for KOH-treated sludge is likely due to physisorbed moisture and/or O-H (alcohol) group as a result of its basic and hygroscopic surface. Treatment using HCl introduces carbonyl compound (quinone or conjugated ketone) on the adsorbent surface as observed by a sharp peak at 1690 cm^{-1}. It also has a peak in the region of 1200-1400 cm^{-1}, that corresponds to the presence of alcohol group (O-H in-plane bend). The presence of acidic oxygen functional groups on the adsorbent surface may enhance the removal of cationic dyes (Zaini *et al*., 2013). The adsorption <1000 cm^{-1} is a finger print zone which corresponds to sulphur and phosphate group.

Adsorption of rhodamine B: Figure 2 shows the effect of initial concentration of rhodamine B on the removal performance of adsorbents. Generally, KOH-treated sludge exhibits a higher percentage of rhodamine B

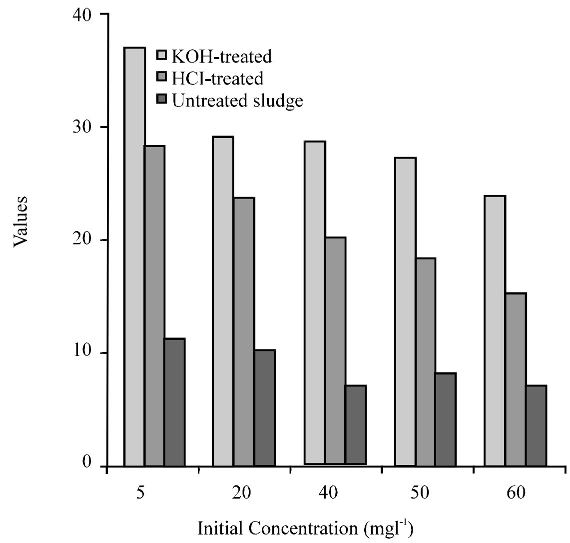

Fig. 2: Effect of initial concentration on the removal of rhodamine B by adsorbents

removal at all concentrations studied. The removal of dye is likely to be strongly influenced by the specific surface area of adsorbent. A higher specific surface area means a greater active sites for possible interactions between the dye molecules and the adsorbent surface. However, the removal performance was found to decrease with increasing dye concentration. Similar pattern was also observed for the other two adsorbents. It indicates that the sludge-adsorbents are only feasible for dye removal at lower concentrations. As the concentration becomes higher, the removal performance becomes less effective because there is only small dye uptake compared to the dye amount in solution.

Figure 3 shows the equilibrium adsorption of rhodamine B by sludge adsorbents. The adsorption of rhodamine B gradually increased with increasing equilibrium concentration. The observed values maximum removal are 14.4, 9.23 and 4.27 mg g^{-1} for KOH-treated, HCl-treated and untreated sludge adsorbents, respectively. The adsorption data were analyzed using three isotherm models andthe isotherm constants are tabulated in Table 2. From Table 2, the adsorption data by three adsorbents were fitted to all models with considerably good SSE and R^2 values. However, the Langmuir model shows a better fit to the adsorption data except for that of the untreated sludge adsorbent. This is supported by the Redlich-Peterson constant g values equal to one. The Langmuir model suggests that the adsorption is favourable with monolayer coverage of the adsorbate (dye) on the adsorbent surface. In addition, this model also signifies the possibility of chemical-type adsorption. In other words, the surface functional groups (especially that of acidic oxygen groups) could in some

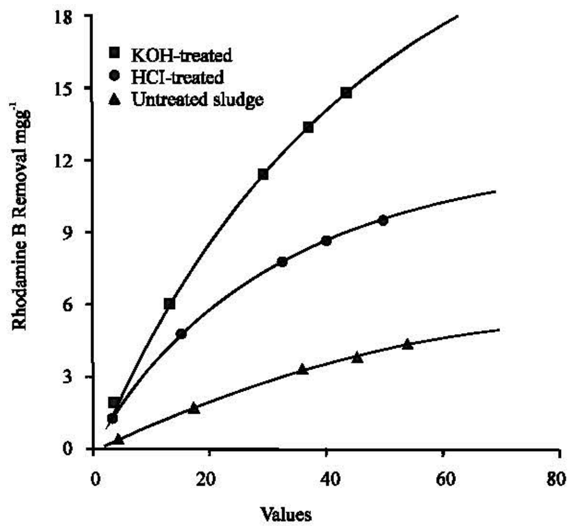

Fig. 3: Equilibrium adsorption of rhodamine B (Lines were predicted by Langmuir model)

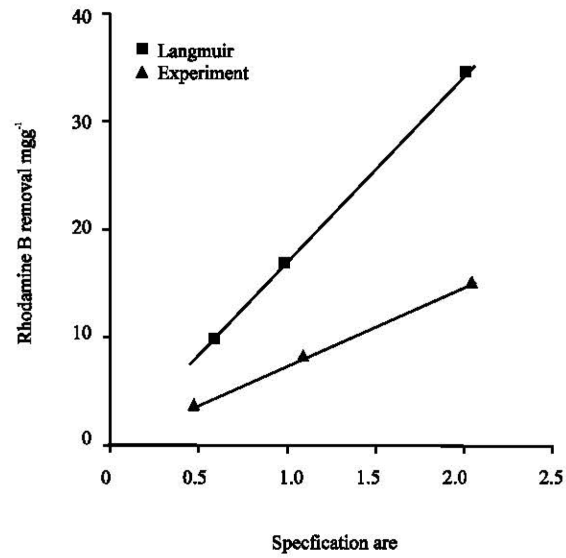

Fig. 4: Effect of specific surface area on the removal of rhodamine B

Table 2: Constants of isotherm models

Models	Untreated sludge	KOH-treated	HCl-treated
Langmuir model			
Q (mgg^{-1})	11.0	35.5	15.9
b (Lmg^{-1})	0.0115	0.0161	0.0300
SSE	0.317	1.473	0.376
R2	0.967	0.988	0.992
Freundlich model			
K (mgg^{-1})(Lmg^{-1})$^{1/n}$	0.216	0.921	0.910
n	1.34	1.36	1.65
SSE	0.301	2.426	1.270
R2	0.968	0.980	0.973
Redlich peterson			
A (Lg^{-1})	0.247	0.570	0.477
B	0.400	0.016	0.030
g	0.419	1.00	1.00
SSE	0.298	1.47	0.376
R^2	0.969	0.988	0.992

Table 3: Rhodamine B removal by various adsorbents

Adsorbent	Surface area (m^2 g^{-1})	Maximum uptake (mgg^{-1})	Reference
Treated parthenium biomass	-	59.2	(Bonel, 1972)
Modified tannery waste	-	250	(Butt and Graf, 2003)
Bagasse pitch activated carbon	-	104	(Crini, 2006)
Carbonaceous industrial waste	-	91.1	(Calvete *et al.*, 2009)
Sago waste carbon	-	16.2	(Cestari *et al.*, 2008)
Carnauba leaves treated with $CaCl_2$	431	40.0	(Da Silva Lacerda *et al.*, 2015)
Carnauba leaves treated with H_3PO_4	402	36.0	(Da Silva Lacerda *et al.*, 2015)
Macauba leaves treated with H_3PO_4	371	33.7	(Da Silva Lacerda *et al.*, 2015)
Pine nut shell treated with H3PO4	296	33.1	(Da Silva Lacerda *et al.*, 2015)
KOH-treated oil-rich sludge	2.08	14.4	This research

way andto certain extent contribute in the binding (anchoring) of rhodamine B to the surface. From Table 2, it is obvious that the values of maximum removal (as determined by the Langmuir model, Q) are higher than the experimental ones. The Langmuir model predicts that there is more rhodamine B uptake could be obtained at higher concentration. However, as early shown in Fig. 3, it is not practical to go for higher dye concentration because the adsorption shall end up with lower performance even though the uptake capacity is expected to increase. The Langmuir constant b for HCl-treated sludge is nearly twice that of KOH-treated sludge. The constant b indicates the affinity of adsorption, or in other words a strong uptake at lower concentration. This could be attributed to the rich surface acidic functional groups in HCl-treated sludge. Figure 4 illustrates the relationship between the specific surface area and the removal of rhodamine B. From Fig. 4, good linear relationship from origin with regression above 0.9 was attained between the specific surface area and the rhodamine B uptake. Thus, it is suggested that the adsorption is mainly governed by the textural characteristics (surface area and porosity) of adsorbent andmay be supported in part by the surface acidic oxygen functional groups. Table 3 summarizes the adsorption of rhodamine B by some adsorbents. It shows that the performance (experimental) of KOH-treated sludge is somewhat lower than the adsorbents reported literature. Yet, they are comparable for the value predicted by the Langmuir model (35.5 mg g^{-1}), even though the specific surface area of the adsorbent used in this work is inferior. Nevertheless, the removal percentage would become lower andit is therefore not practical to achieve a higher adsorption capacity at a higher rhodamine B concentration.

CONCLUSION

Oil-rich sludge was converted into adsorbents for rhodamine B removal. The chemically treated adsorbents demonstrate an improved removal performance compared to the untreated one. The adsorption of rhodamine B shows a linear correlation to the specific surface area of adsorbent. The acidic oxygen functional groups could also play some role in the adsorption. HCl-treated sludge exhibits a higher adsorption affinity for rhodamine B, while KOH-treated sludge shows a higher maximum removal compared to other adsorbents studied. Nevertheless, the adsorption process is recommended for lower concentration as a higher concentration would inevitably lead to the decrease in removal percentage.

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