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Bio-polishing sludge adsorbents for dye removal

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The objective of this work is to evaluate the removal of methylene blue dye by bio-polishing sludge-based adsorbents. The adsorbents were characterized according to the specific surface area, pH upon the treatment and surface functional groups. The adsorption of dye was carried out at room temperature, and the adsorption data were analyzed using the isotherm and kinetics models. The bio-polishing sludge is rich in ash content, and the presence of surface functional groups varied with the treatment strategies. The specific surface area of adsorbents is between 7.25 and 20.8 m^2/g. Results show that the maximum removal of methylene blue by sludge adsorbents was observed to have the following order: untreated sludge (SR) > zinc chloride-treated (SZ) > microwave-dried (SW) = potassium carbonate-treated (SK) > acid-washed (SH). The maximum adsorption capacities for SR and SZ as predicted by the Langmuir model are 170 and 135 mg/g, respectively. Although SR demonstrates a higher maximum removal than SZ, the latter exhibits greater removal intensity and rate constant even at high dye concentration. The bio-polishing sludge is a promising adsorbent for dye wastewater treatment.

Keywords: adsorption, adsorbent, bio-polishing sludge, methylene blue, chemical treatment.

INTRODUCTION

Malaysia is one of the largest producers of palm oil in the world. Currently, there are more than 426 mills in the country[1]. In wet milling oil extraction, about 5–8 tons of water are consumed for every ton of crude palm oil produced; more than 50% of this water ends up as effluent[2]. Nearly 55×10^6 m^3 of palm oil mill effluent is generated from the palm oil industry every year[3]. Of this, 48000 mg/L is solids commonly known as palm oil mill effluent sludge[4]. The sludge produces bad odours, and is a source of surface and ground pollution[4, 5]. Thus, it generally requires special handling and treatment prior to discharge.

The palm oil mill effluent sludge originates in leaves, trunk, decanter cake, empty fruit bunches, seed shells and mesocarp fibre[3, 4]. Because of its high nutrient content, some studies recommended composting as an eco-friendly solution to the sludge problems[4, 6]. However, the derived compost could release phyto-toxic substances such as ammonia, ethylene oxide and organic acids that are detrimental to plants growth[4].

The search for alternative approach to sludge handling and disposal has become a subject of considerable interest. It is postulated that large loads of sludge can be reduced if it can be converted into useable material such as adsorbent. The utilization of sludge as adsorbent could overcome the central associated problems, and further it could also be applied to remove wide range of pollutants in water[5, 7, 8].

Bio-polishing is the final biological treatment of palm oil mill effluent prior to discharge. Because of the complex nature of this treatment, the solid residue may exhibit unique attributes as compared to other sources of sludge[7]. To date, the use of bio-polishing sludge as potential adsorbent is still widely unexplored in much of published literature[5, 8]. Therefore, the present work was aimed at evaluating the adsorptive characteristics of this sludge and its adsorbent derivatives. Methylene blue dye solution was used as a probe to establish the removal performance. The equilibrium and kinetics data were analyzed using the established models, and the possible removal mechanisms were discussed.

MATERIAL AND METHODS

Material

Bio-polishing sludge was obtained from the final biological treatment of mill effluent at Felda Taib Andak, Johor state of Malaysia. Methylene blue dye powder (CAS No. 61-73-4; $C_{16}H_{18}ClN_3S$, molecular weight = 319.85 g/mol, assay 98.5%) was supplied by HmbG Chemicals. All chemicals are of analytical-reagent grade.

Preparation of adsorbents

The sludge was ground and sieved to an average size of 500 μm. It was washed with running tap water to remove dirt and debris until the residual water becomes clear. After that, the sludge was washed and rinsed with distilled water, and dried at 110°C in oven.

The dried sludge was chemically treated with zinc chloride ($ZnCl_2$) and potassium carbonate (K_2CO_3) solutions at solid impregnation ratio (w/w) of 1.0. The mixtures were dried in a 800 W microwave oven at 70% power intensity for 10 minutes. The chemically-treated solids were soaked in 3 M HCl overnight to remove impurities and residual chemicals, after which they were washed several times in distilled water to a constant pH. The same procedures were repeated for oven-dried and microwave-dried sludge (in water). The resultant adsorbents were designated as SH, SW, SZ and SK for acid-washed (oven-dried), microwave-dried (in water), $ZnCl_2$-treated and K_2CO_3-treated sludge adsorbents, respectively.

The untreated sludge, designated as SR was also employed in the adsorption studies. The sludge ash, designated as SA was prepared through the pyrolysis of untreated sludge in furnace at 850°C for 4 h. The adsorbents, SR and SA were used without further treatment. All adsorbents were dried before the characterization and adsorption studies.

Characterization of adsorbents

The specific surface area of adsorbents was measured using surface area analyzer (Pulse ChemiSorb 2705, Micrometrics) at liquid nitrogen temperature of 77 K. The available surface functional groups were determined by a KBr pellet method using Fourier transform infrared (FTIR) instrument (Spectrum™ One spectrometer, PerkinElmer).

Batch adsorption studies

The stock solution of methylene blue was prepared by dissolving desired weight of methylene blue powder in distilled water. It was diluted to different initial concentrations between 10 and 300 mg/L for batch adsorption studies.

About 0.05 g adsorbent was brought into intimate contact with 50 mL of methylene blue solution of different initial concentrations. The mixture was allowed to equilibrate on orbital shaker at 120 rpm and room temperature for 72 h. The initial solution pH was not adjusted, and the values were recorded as 5.1 ±0.2. The final pH was measured at equilibrium. The residual dye concentration was measured using Biochrom Libra S6 spectrophotometer at a wavelength of 672 nm. The equilibrium removal of methylene blue, q_e (mg/g) was calculated as,

$$q_e = \frac{(C_o - C_e)}{m} V \tag{1}$$

where C_o and C_e (mg/L) are the initial and equilibrium concentrations, respectively, V (mL) is the volume of dye solution and m (g) is the mass of dry adsorbent.

Three isotherm models, namely Langmuir[9, 10], Freundlich[11] and Redlich-Peterson[12] were used to describe the adsorption data. The Langmuir isotherm is commonly used to explain monolayer adsorption onto a completely homogeneous surface, and is given as,

$$q_e = \frac{QbC_e}{1 + bC_e} \tag{2}$$

where Q (mg/g) is the maximum uptake per unit mass of adsorbent to form a complete monolayer on the surface of adsorbent, and b (L/mg) is a constant related to the affinity of the binding sites. The empirical Freundlich isotherm is based on the sorption on a heterogeneous surface, and is given by,

$$q_e = K_F C_e^{\frac{1}{n}} \tag{3}$$

where K_F and $1/n$ are the Freundlich constants related to the maximum adsorption capacity and intensity, respectively. The $1/n$ value ranging from 0 to 1 signifies the surface heterogeneity, while the n value ranging between 2 and 10 represents a favourable adsorption process. The Redlich-Peterson model is a hybrid isotherm that combines both features of Langmuir and Freundlich equations, and is given as,

$$q_e = \frac{AC_e}{1 + BC_e^g} \tag{4}$$

where A, B and g are the Redlich-Peterson constants, and $0 < g < 1$. The equation reduces to Henry's law when g is equal to 0, while it becomes Langmuir isotherm when g is unity.

The sludge adsorbents with appreciable methylene blue uptake were chosen for rate of adsorption study at selected methylene blue concentrations. About 0.25 g adsorbent was added into a 250 mL of methylene blue solution. The residual methylene blue concentration was measured at preset time intervals. The up-scaling factor of five was employed to ensure that the system is not entirely upset when the solution was withdrawn for measurement.

The rate of adsorption data were evaluated using kinetics models, namely the pseudo-first-order[13] and pseudo-second-order[14] models. The pseudo-first-order model is given by,

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{5}$$

where q_t (mg/g) is the amount adsorbed at time t (min), and k_1 (min^{-1}) is the pseudo-first-order rate constant. The applicability of this model indicates that the external diffusion is a significant step. The pseudo-second-order equation is based on chemical-related adsorption, and is given as,

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{6}$$

where k_2 (g/mg·min) is the pseudo-second-order rate constant. The initial adsorption rate, h (mg/g·min) as t approaching zero is expressed as,

$$h = k_2 q_e^2 \tag{7}$$

The isotherm and kinetics models were solved using *Solver* add-in of MS Excel, given the condition where the sum of squared error (*SSE*) is the least rendering the optimum correlation of determination (R^2).

RESULTS AND DISCUSSION

Characteristics of adsorbents

The ash content of bio-polishing sludge was recorded as 45%, while the yields of other treated sludge-based adsorbents are between 33 and 55% due to some losses during the treatment procedures and washing. All chemically-treated and acid-washed adsorbents show a comparable pH between 3.3 and 3.9, while the sludge ash (SA) and untreated sludge (SR) possess a higher pH of 6.6 and 7.4, respectively. The values of specific surface area were recorded as 9.12, 14.8, 15.8, 18.7, 20.8 and 7.25 m^2/g for $ZnCl_2$-treated (SZ), K_2CO_3-treated (SK), microwave-dried (SW), untreated sludge (SR), HCl-washed (SH) and sludge ash (SA), respectively. These values are undoubtedly inferior when compared to that of commercial activated carbon[8]. The specific surface area was found to decrease after the treatment procedures except for the direct treatment with hydrochloric acid (SH). It is likely that the clogged pores are accessible due to partial demineralization of sludge by HCl, whereas the other treatment methods could result in the collapse of existing pores[8, 15]. Nevertheless, this variation is not too significant from the viewpoint of porous texture development.

Figure 1 shows the FTIR spectra of bio-polishing sludge adsorbents. All six adsorbents display a broad peak centred between 3600 and 3200 cm^{-1} indicating the

presence of physisorbed moisture. The carbon backbone structure (alkanes) explains the narrow band ranging from 2980 to 2800 cm^{-1}. Another broad peak at 1724–1510 cm^{-1} signifies the presence of carboxylic acids, alkenes and arenes, *i.e.*, the characteristics of humic substances, the main organic constituents of sludge[5, 8]. This could be supported by peaks with small intensity varying from 805–705 cm^{-1}. However, the peaks centred at 1650 cm^{-1} show a decreasing intensity according to the order: SR > SK > SH = SW > SZ, which is probably due to the decomposition and/or degradation of some carbon compounds and functional groups upon the treatment strategies.

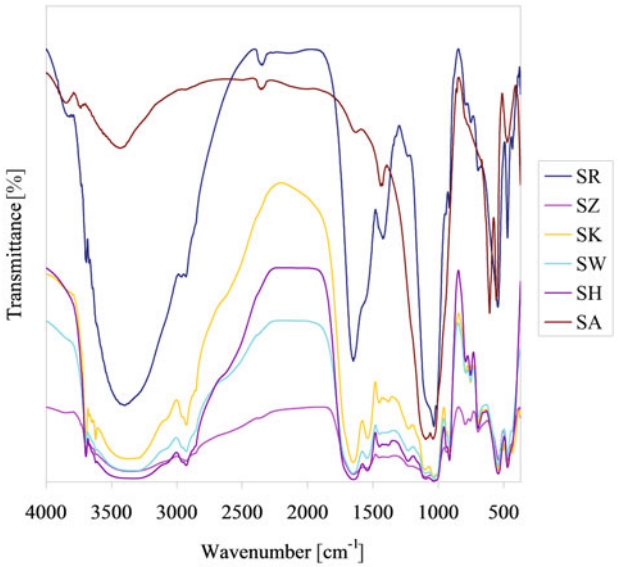

Figure 1. FTIR spectra of sludge adsorbents

All adsorbents also demonstrate a common peak centred at 985 cm^{-1} that corresponds to the presence of silica in ash[8]. The decreasing peaks intensity indicates that the silicon function was partly removed from the chemically-treated and acid-washed adsorbents[15, 16]. The sludge ash (SA) exhibits the absence of important surface functional groups due to the elimination of volatiles after pyrolysis at higher temperature. The presence of bromide in the main fingerprint spectral region is due to KBr in FTIR analysis.

Removal of methylene blue

Figure 2 shows the removal of methylene blue by adsorbents derived from bio-polishing sludge. In general, the adsorbents display an increasing removal of methylene blue with increasing initial concentration. The equilibrium pH was found to be similar with the pH of adsorbents. The increase of concentration offers the driving force for methylene blue molecules to overcome the adsorbent-phase mass transfer resistance, thus allowing more active sites to be filled. This is true until the adsorption sites are completely occupied or the saturation point has been attained, at which there will be no further increase in adsorption capacity with increasing concentration.

From Figure 2, the untreated sludge (SR) exhibits a greater methylene blue removal of 145 mg/g at initial concentration of 268 mg/L. At this concentration, the adsorption capacity was observed to have the following

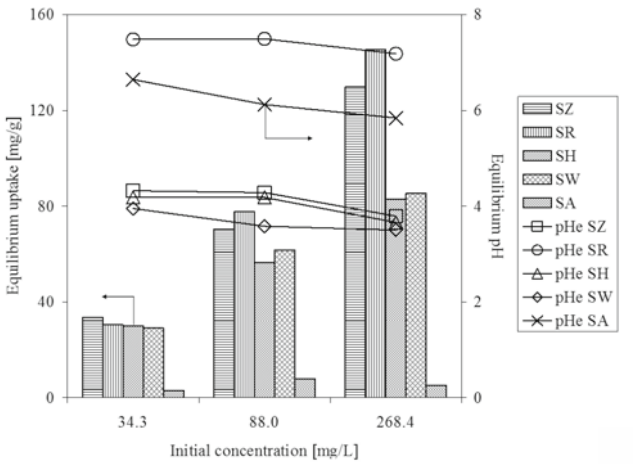

Figure 2. Effect of initial concentration on methylene blue removal by sludge adsorbents

order: SR > SZ > SH = SW > SA. It implies that the treatment procedures could in some way diminish the active sites on the sludge surface, thus decreasing the removal capacity (Fig. 1). However, a greater methylene blue removal by SZ as compared to other chemically-treated counterparts is possibly due to the use of $ZnCl_2$ that enhances the surface affinity of ash-rich sludge for adsorption[8, 15, 17]. The result also reveals that the removal of methylene blue is not driven by specific surface area of adsorbents.

Sludge ash (SA) demonstrates a lower methylene blue removal capacity. It indicates that sludge ash (without treatment) does not have much to offer in the adsorption of methylene blue. In a related work, Zaini and co-workers[18] reported a 51 mg/g removal of methylene blue resulting from a tenfold increase in specific surface area of ash (163 m^2/g) after hydrochloric acid treatment. Generally, a significant increase in specific surface area of adsorbent for favourable adsorption could be achieved by acid treatment. However, the presence of organic substances in bio-polishing sludge may inhibit the access to the pore channels for increasing the specific surface area by acid treatment.

Adsorption isotherm

Three isotherm models were used to describe the adsorptive behaviour of adsorbents. Figure 3 represents the equilibrium adsorption of methylene blue onto bio-polishing sludge adsorbents, and the isotherm constants are tabulated in Table 1.

From Figure 3, the adsorbents display a reasonably good removal efficiency of more than 95% at equilibrium concentration below 5 mg/L. At this point onwards, each adsorbent demonstrates an increasing pattern of methylene blue adsorption, and levels off at different values. The concave downward curve, *i.e.*, increasing adsorption with decreasing gradient indicates a favourable adsorption.

The maximum methylene blue adsorption were observed to have the following order: SR > SZ > SK = SW > SH. It is interesting to note a greater methylene blue removal by SZ as compared to that of SR at equilibrium concentrations between 5 and 20 mg/L. This could be associated with high affinity of SZ to attract methylene blue molecules especially at lower concentrations. Nevertheless, SR possesses a greater maximum capacity

Table 1. Isotherm constants of methylene blue removal by sludge adsorbents

Isotherm model	Sludge adsorbent				
	SR	SH	SZ	SK	SW
Langmuir					
Q (mg/g)	170	83.2	135	97.4	98.8
b (L/mg)	7.24×10^{-2}	0.162	0.446	6.37×10^{-2}	6.36×10^{-2}
SSE	433	380	1049	412	478
R^2	0.985	0.945	0.963	0.961	0.959
Freundlich					
K_F (mg/g)/(L/mg)$^{1/n}$	25.2	22.0	44.5	19.0	19.1
n	2.63	3.69	4.21	3.20	3.21
SSE	2654	265	1130	40.8	342
R^2	0.905	0.955	0.951	0.994	0.964
Redlich-Peterson					
A (L/g)	12.3	51.9	162	198	27.4
B	7.24×10^{-2}	1.64	2.27	9.53	0.988
g	1	0.803	0.863	0.706	0.760
SSE	433	158	513	31.7	271
R^2	0.985	0.972	0.977	0.995	0.971

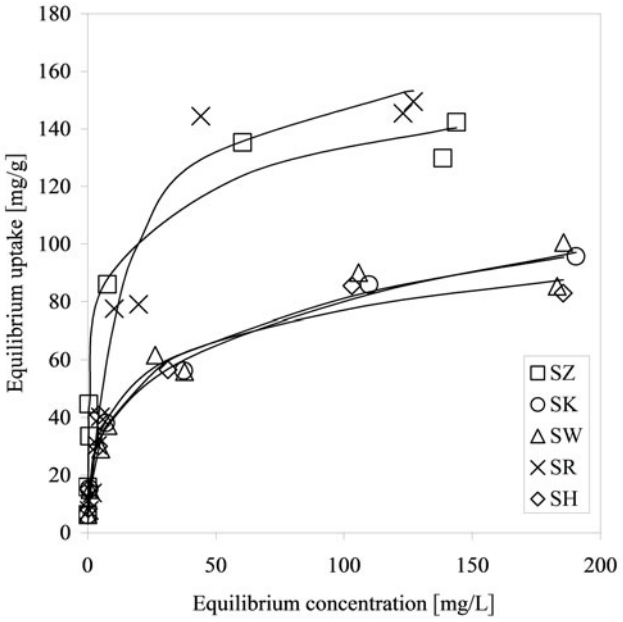

Figure 3. Equilibrium adsorption of methylene blue by sludge adsorbents (lines were predicted by the Redlich-Peterson model)

among the adsorbents studied. It indicates a benefit of using the untreated sludge – a valueless material with minor cost implications – for wastewater treatment.

All isotherm models are sufficient to describe the behaviour of methylene blue removal by sludge adsorbents (Table 1). However, the equilibrium data are more fitted to the Redlich-Peterson model because of lower *SSE* values and R^2 approaching unity. It is suggested that the adsorption is monolayer, but happens on the heterogeneous surface. This removal mechanism is supported by the g values greater than 0.7, and the n^{-1} values ranging between 0.2 and 0.4. Moreover, a greater adsorption intensity of SZ is depicted by a higher Langmuir constant, b. In addition, SH also possesses a comparably good adsorption intensity that could be attributed to high specific surface area.

Adsorption kinetics

Two sludge adsorbents, namely SR and SZ were evaluated for adsorption kinetics because of the substantial removal of methylene blue among the adsorbents studied. The rate of adsorption was analyzed using the pseudo-first-order and pseudo-second order models. Figure 4 shows the kinetics profiles of methylene blue removal by SR and SZ, and the respective rate constants are tabulated in Table 2.

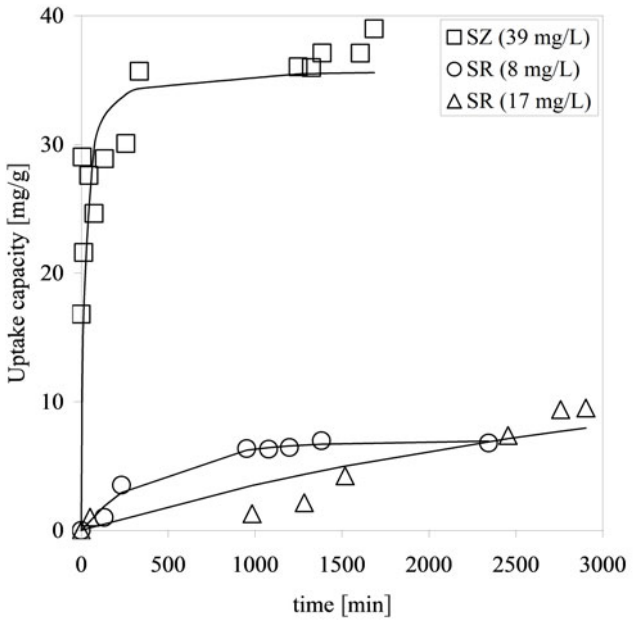

Figure 4. Kinetics profiles of methylene blue removal by selected sludge adsorbents (lines were predicted by the pseudo-second-order model)

From Figure 4, SZ displays a rapid adsorption that reaches equilibrium after 8 h in contact with 39 mg/L of methylene blue solution, whereas a longer period of 17 h is needed by SR to attain the equilibrium for a lower methylene blue concentration of 8 mg/L. It shows that SZ can offer fast decolourization even at higher methylene blue concentration. On the other hand, the

adsorption rate of SR is slower at higher concentration, thus longer contact time would be required to achieve the equilibrium.

From Table 2, the pseudo-first-order and pseudo-second-order models show a reasonably good fit to the experimental data with small variation between the experimental ($q_{e,exp}$) and calculated ($q_{e,cal}$) values. The applicability of these models implies that the adsorption is driven by external diffusion: 1) the adsorbent-phase mass transfer resistance is dominant at lower concentration, and 2) at higher concentration, the mechanism switches to chemical-type adsorption[8].

Table 3 shows the comparison of the pseudo-second order kinetics constants for methylene blue removal by some adsorbents. The trend of rate constant, k_2 for SR as presented in Table 2 is in agreement with some of the published studies; a decreasing rate constant with increasing methylene blue concentration[18, 19, 22, 24, 26, 27]. Although increasing the concentration reduces the solid-phase mass transfer resistance for more adsorption, the number of available active sites progressively decreases with time thus decreasing the adsorption rate. From Table 3, SZ exhibits a comparable, and reasonably high rate constant than the other methylene blue adsorbents.

Table 4 summarizes the maximum capacity of methylene blue by some adsorbents and activated carbons. It is evident that the bio-polishing sludge adsorbents possess lower specific surface area as compared to the other adsorbents. However, SR and SZ demonstrate comparable and better maximum adsorption than some adsorbents with higher specific surface area. It indicates that the methylene blue adsorption by SR and SZ is not specific surface area-dependent, but is likely to be promoted via complex interactions between methylene blue molecules and surface functional groups.

Table 2. Kinetics constants of methylene blue removal by selected sludge adsorbents

Sample	Initial concentration [mg/L]	$q_{e,exp}$ [mg/g]	Pseudo-first order model				Pseudo-second order model				
			$q_{e,cal}$ [mg/g]	k_1 [min^{-1}]	SSE	R^2	$q_{e,cal}$ [mg/g]	k_2 [g/mg·min]	h [mg/g·min]	SSE	R^2
SZ	38.9	38.2	33.9	6.77×10^{-2}	180	0.860	35.9	1.82×10^{-3}	2.35	90.5	0.930
SR	8.2	7.8	6.98	2.37×10^{-3}	1.22	0.979	8.73	2.67×10^{-4}	2.03×10^{-2}	1.87	0.967
	17.4	13.8	13.7	2.96×10^{-4}	16.3	0.860	17.9	1.44×10^{-5}	4.67×10^{-3}	19.3	0.833

Table 3. Pseudo-second order kinetics constants for methylene blue removal by various adsorbents

Sample	Specific surface area [m^2/g]	Initial concentration [mg/L]	$q_{e,cal}$ [mg/g]	k_2 [g/mg·h]
KOH-activated sludge[8]	79	10	5.54	0.0072
HCl-treated sludge ash[18]	163	50	23.5	0.009
HCl-treated sludge ash[18]	163	130	42.9	0.021
Graphene[19]	296	20	41	0.0009
Graphene[19]	296	40	84.8	0.0001
Microwave-modified bamboo charcoal[20]	255	50	17.5	0.120
NaOH-treated coal fly ash[21]	6.92	50	5.71	0.0627 [min]
K_2CO_3-activated mangosteen peel carbon[22]	1099	50	55.1	0.095 [min]
K_2CO_3-activated mangosteen peel carbon[22]	1099	300	279	0.020 [min]
$ZnCl_2$-activated carbon powder[23]	288	50	24.5	0.0707 [min]
$ZnCl_2$-activated carbon powder[23]	288	300	123	0.0082
$FeCl_3$-activated date pits carbon[24]	780	50	90.8	0.0457 [min]
$FeCl_3$-activated date pits carbon[24]	780	350	243	0.0187 [min]
$ZnCl_2$-activated *Enteromorpha prolifera*[25]	1688	100	263	77.2×10^{-6} [min]
Graphene oxide[25]	32	100	244	90.8×10^{-6} [min]
$ZnCl_2$-activated date stones[26]	1046	50	91.3	0.0447 [min]
$ZnCl_2$-activated date stones[26]	1046	350	335	0.0210 [min]
KOH-activated oil palm fiber carbon[27]	1223	50	50.6	0.231 [min]
KOH-activated oil palm fiber carbon[27]	1223	300	283	0.020 [min]
Untreated POME sludge (SR)	18.7	8.20	8.73	2.67×10^{-4} [min]
Untreated POME sludge (SR)	18.7	17.4	17.9	1.44×10^{-5} [min]
$ZnCl_2$-treated POME sludge (SZ)	9.12	38.9	35.9	1.82×10^{-3} [min]

Table 4. Methylene blue removal by various adsorbents

Sample	Specific surface area [m^2/g]	Equilibrium pH	Maximum uptake [mg/g]
NaOH-treated waste activated sludge[5]	–	7.0	66.3
KOH-activated sludge[8]	79	7.5	23.5
HCl-treated sludge ash[18]	163	–	50.7
Graphene [19]	296	–	185
NaOH-treated coal fly ash[21]	6.92	–	34
K_2CO_3-activated mangosteen peel carbon[22]	1099	6.3	380
$ZnCl_2$-activated carbon powder[23]	288	6.1	154
$FeCl_3$-activated date pits carbon[24]	780	–	249
$ZnCl_2$-activated *Enteromorpha prolifera*[25]	1688	6.0	270
Graphene oxide[25]	32	6.0	244
$ZnCl_2$-activated date stones[26]	1046	–	369
KOH-activated oil palm fiber carbon[27]	1223	–	380
KOH-activated oil palm empty fruit bunch[28]	1372	–	395
NaOH-treated rice husks activated carbon[29]	1015	–	413
K_2CO_3-activated wood sawdust[30]	1496	–	423
Cotton-made activated carbon fiber[31]	2060	7.0	597
KOH-activated coconut husk[32]	1356	–	418
Untreated blast furnace sludge[33]	31.5	7.0	70.6 [C_o = 160 mg/L]
Untreated POME sludge (SR)	18.7	7.4	170
$ZnCl_2$-treated POME sludge (SZ)	9.12	4.0	135

CONCLUSION

Six adsorbents were derived from bio-polishing sludge. The untreated sludge (SR) shows a higher adsorption of methylene blue than the other adsorbents. However, the adsorption rate of zinc chloride-treated sludge (SZ) is more rapid than that of the untreated sludge. The possible mechanisms of adsorption could be summarized as follows: 1. monolayer methylene blue adsorption on the heterogeneous adsorbent surface, 2. external diffusion to overcome adsorbent-phase mass transfer resistance at lower concentration, 3. chemisorption at higher concentration, and 4. complex interactions between methylene blue molecules and surface functional groups. Through simple treatment with minimum cost implications, bio-polishing sludge can be a useful and promising adsorbent for dye decolourization from wastewater.

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