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Comparison of Remazol Black B biosorptive properties of live and treated activated sludge

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ABSTRACT

Biosorption of Remazol Black B, a vinyl sulfone type reactive dye, from aqueous solution was investigated to compare the binding capacities of untreated (live) and treated (dried, autoclaved, acid (H_2SO_4)-treated, base (NaOH)-treated) activated sludge in this study. Remazol Black B uptake was strongly affected by the solution pH and optimum adsorption pH value was determined as 2 for all the live and treated activated sludge biosorbents. It was seen that the sorption capacity of each biosorbent enhanced with decreasing temperature. Dye uptake also increased with increasing initial dye concentration up to 500 mg l^{-1} for each biomass type. Contrary to assumption it is found that all the treatment methods diminished the dye biosorption capacity of activated sludge. Among the five biosorbents, live activated sludge had a maximum dye uptake capacity of 134.8 mg g^{-1} at 25 °C. The Langmuir–Freundlich adsorption model described the equilibrium data of each dye–biosorbent system accurately in the concentration and temperature ranges studied. The pseudo-second-order adsorption model defined the overall adsorption kinetics of each biosorption process exactly.

1. Introduction

The impact and toxicity of dyes that are released in the environment are very important and have been extensively studied. The source of such pollution lies in the rapid increase in the use of synthetic dyes because of their ease of use, inexpensive cost of synthesis, stability and variety of colour compared with natural dye [1]. During the processing of dye manufacturing and dye application, up to 15% of the used dyestuff are released into the process water so the effluents from these industries are highly coloured [2–4]. Standard wastewater treatments for colour removal appeared ineffective because of the chemical stability of most dye pollutants that makes them non-biodegradable. This led to the study of other effective methods, and many physical and chemical treatment methods including adsorption, chemical coagulation, precipitation, filtration, electrodialysis, and oxidation have been used for the treatment of dye-containing effluents. Some of these techniques have been shown to be effective, although they have limitations [5].

Reactive dyes are typically azo-based chromophores combined with different types of reactive groups, e.g., vinyl sulfone, chlorotriazine, trichloropyrimidine, difluorochloropyrimidine. Azo reactive dyes are characterized by the presence of one or more –N=N–(azo) bonds. They have bright colour, excellent colour-fastness, simple application techniques and low energy consumption. Almost 45% of all textile dyes produced annually belong to the reactive class as a consequence of an intensive use of these dyes for colouring cellulose and viscose-rayon fibres. Reactive dyes have been identified as problematic compounds in textile wastewaters because they are water-soluble, are found in the wastewater at higher concentrations than other dye classes and mainly in their spent, hydrolysed form, and cannot be easily removed by conventional treatment systems [1–6].

Biosorption can be defined as sequestering of organic and inorganic species including metals, dyes and odour causing substances from aqueous solutions using live or dead biomass or their derivatives [6,7]. This biomass may be bacteria, fungi, algae, sludges from biological wastewater treatment plants, and by-products from fermentation industries or seaweeds [6,8–17]. “Biosorption” term is used to indicate a number of metabolism-independent processes (physical and chemical adsorption, ion exchange, complexation, chelation and micro-precipitation) taking place essentially in the cell wall. Microbial cell surfaces carry various types of functional groups, which are responsible for the sequestration of hazardous materials from aqueous solution. This technology has an advantage of low operating cost, is effective in treating dilute solutions and generates minimum amounts of effluent. Since the biosorption of dye ions takes place mainly on the biomass surface, increasing the sorption active sites on the surface by pre-treatment would be an effective approach to enhance the dye sorption capacity of the biosorbent. Pre-treatments could modify the surface characteristics/groups either by removing or masking the groups or by exposing more dye-binding sites. Physical pre-treatment methods

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include drying, vacuum and freeze-drying, boiling or heating, autoclaving, mechanical disruption. Chemical pre-treatment methods include treatment with various organic (formaldehyde, ethanol, acetone, etc.) and inorganic (NaOH, H_2SO_4, HNO_3, $NaHCO_3$, $CaCl_2$, etc.) chemicals. Many studies have focused on enhancing the active binding sites to improve the biosorption. However, it must be paid attention for selecting appropriate chemical and/or physical methods for pre-treatment. Some methods, such as alkali treatment are found to improve dye biosorption to some extent whereas acid treatment of biomass is found to have almost negative influence on dye biosorption. On the other hand, heat treatment of biomass has been shown to increase the dye uptake capacity significantly in some cases [6,9,13,14,17–19].

Sewage sludge can be defined as the residue generated from the treatment of wastewater. The two principal types of sludges are primary sludge and secondary sludge. Primary sludge constitutes the material collected from the primary settling tanks employed in wastewater treatment plants. Secondary sludge, also known as biological (activated) sludge, constitutes the sludge generated from the biological treatment of the wastewater drained from the settling tanks. Activated sludge is a well-known biomass used for the purification of some industrial effluents and domestic wastes. Probably the most abundant source of mixed microbial biomass is the activated sludge wastewater treatment process. Activated sludge from wastewater systems contains mainly bacteria, protozoa and extra-cellular polymeric substances (EPS). The functional groups on bacteria, protozoa and EPS, such as, acidic polysaccharides, carboxyl, phosphonate, amine, hydroxyl groups and other components, provide binding sites for dye biosorption [11–16,20]. Part of the microorganisms over grown in such wastewater systems can be separated and utilized for the removal of dye ions as an abundant and cheaper biosorbent.

The key objectives of this paper are to compare the adsorption capacities of the resting and physically and chemically treated activated sludge for Remazol Black B dye, used extensively in textile industry in Turkey, and to discuss the kinetics and equilibrium data of Remazol Black B biosorption. This is the first study to compare the effect of various pre-treatments onto activated sludge biomass for Remazol Black B dye removal from aqueous solution.

2. Materials and methods

2.1. Microorganism

A secondary sludge, which was collected from ASKI, Ankara Municipal Wastewater Treatment Plant, Turkey, was used as a low-cost biosorbent in the removal of reactive dye Remazol Black B from aqueous solution. The sludge was centrifuged at 5000 rpm for 5 min, then washed thoroughly several times with distilled water and re-centrifuged. A part of the centrifuged sludge was used directly in biosorption experiments as live biomass. The remaining part was inactivated by the following physical and chemical pre-treatment methods.

For the biosorption studies with heat-treated activated sludge, a part of centrifuged sludge was oven dried at 60 °C to constant weight. Some of the centrifuged sludge was also killed by autoclaving at 121 °C and 1.2 bar for 15 min. A separate set of biosorption experiments were done with chemically treated activated sludge. For this purpose, a part of centrifuged sludge (50 g) was mixed with 100 ml 0.5 M H_2SO_4 solution and agitated for 1 h. Native sludge (50 g) was also inactivated by treating with 100 ml 1 M NaOH for 1 h. After each pre-treatment the sludge was washed twice with distilled water, re-centrifuged and dried at 60 °C to constant weight.

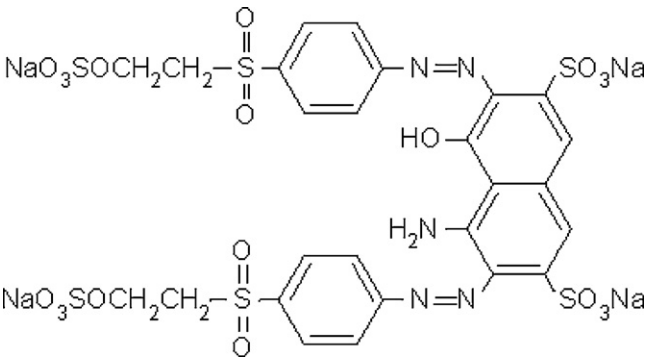

Fig. 1. Structure of Remazol Black B dye.

2.2. Preparation of untreated and treated activated sludge and Remazol Black B solutions for biosorption

A weighed amount of untreated (live) biomass was suspended in distilled water at a concentration of 10 g l^{-1} on a dry weight basis and used directly for Remazol Black B biosorption. For the biosorption studies with the treated sludge, a known quantity of treated biomass suspended in distilled water was homogenized for 30 min in a homogenizer (Janke and Kunkel, IKA-Labortechnick, Ultra Turrax T25) at 8000 rpm for 20 min, diluted to a known volume, and then stored in the refrigerator. 10 ml of treated biomass suspension was contacted with 90 ml of solution containing a known concentration of Remazol Black B in an Erlenmayer flask at the desired temperature and pH. All the final solutions contained 1 g l^{-1} of sorbent.

Remazol Black B (C.I. Reactive Black 5) (empirical formula $C_{26}H_{21}O_{19}N_5S_6Na_4$; molecular weight = 991.8), a commercial diazo reactive dye containing two-vinyl sulfone as reactive groups (structure of the dye was shown in Fig. 1), was kindly supplied by Gemsan, Turkey, and used as received without further purification.

The test solutions containing required dye concentration were prepared by diluting 1 g l^{-1} of stock solution of dye, which was obtained by dissolving weighed amount in 1 l of double-distilled water. The range of concentrations of prepared dye solutions changed between 25 and 500 mg l^{-1}. The initial pH of each test solution was adjusted to the required value with H_2SO_4 and NaOH solutions at different concentrations changing from 0.01 to 1 M before contacting the live biosorbent or biosorbent solution. The preliminary studies showed that the initial pH value did not change considerably during the experimental period.

2.3. Biosorption experiments

Sorption studies were conducted in a routine manner by the batch technique. A number of plugged Pyrex glassed Erlenmeyer containing a definite volume (100 ml in each case) of solutions of Remazol Black B dye at desired concentration, pH and temperature were placed in a thermostatic rotary shaker. The flasks were continuously agitated on a shaker at 150-rpm constant shaking rate for 24 h to ensure that equilibrium was reached. Samples (5 ml) were taken before mixing the live sorbent/sorbent solution and dye bearing solution and at definite time intervals. Before analysis the samples were centrifuged at 5000 rpm for 3 min and the supernatant fraction was analyzed for the remaining dye ions. All the biosorption experiments were repeated twice to confirm the results. The data were the mean values of two replicated determinations. For the use of average value, the percent relative standard deviation for samples was calculated and if the value of standard

deviation for any sample was greater than 10% the data were not used.

The uptake of dye by unit mass of biosorbent at any time (q) was determined from Eq. (1):

$$q = \frac{C_o - C_{res}}{X} \quad (1)$$

where C_o is the initial Remazol Black B concentration (mg l^{-1}), C_{res} is the residual Remazol Black B concentration at any time (mg l^{-1}) and X is the sorbent concentration (g l^{-1}). C_{res} is equal to C_{eq} and q is equal to q_{eq} at equilibrium.

2.4. Analysis of Remazol Black B

The residual Remazol Black B concentration in the biosorption medium was determined spectrophotometrically. The absorbance of the colour was read directly or after a proper dilution at 597 nm where the maximum absorption peak exists using Labomed Inc. (USA) spectrophotometer with a matched pair of glass cuvettes having 1 cm optical lengths. The dye concentration was determined using a standard curve of absorbance versus known dye concentration.

3. Results and discussion

The comparative Remazol Black B biosorption properties of untreated and treated activated sludge biosorbents were investigated as a function of initial pH, temperature and initial Remazol Black B concentration. The results are given as the units of adsorbed dye quantity per gram of dried biomass at any time (q: mg g^{-1}) or at equilibrium (q_{eq}: mg g^{-1}) and unadsorbed dye concentration in solution at equilibrium (Ceq: mg l^{-1}) and removal % (defined as the ratio of adsorbed concentration of Remazol Black B at equilibrium to the initial concentration of Remazol Black B).

3.1. Effect of initial pH on Remazol Black B biosorption

Earlier studies on dye biosorption have shown that the pH of the aqueous solution is one of the most important variables, which controls the biosorption process by affecting the nature of the surface charge of the biosorbent at water interface and the speciation of the adsorbate in the water [6,12,21]. Experiments were performed to investigate the effect of initial pH on the biosorption of Remazol Black B at various pH values ranging from 1 to 6 for each untreated and treated activated sludge biomass–dye system. For each pH value, the dye concentration (100 mg l^{-1}), biosorbent dosage (1 g l^{-1}) temperature (25 °C) and shaking rate (150 rpm) were kept constant. The variation of Remazol Black B removal with initial pH was given in Fig. 2 for each biosorbent. Fig. 2 shows that the uptake of Remazol Black B as a function of initial pH by all treated sludges is similar in pattern to that by the live biomass. The equilibrium uptake of anionic dye enhanced notably with raising the pH up to 2 and declined sharply above pH 2 for all the fresh and treated activated sludge biomasses. Fig. 2 also indicates that physical and chemical treatments of the live sludge alter their Remazol Black B uptake capacities due to initial pH. Generally the equilibrium Remazol Black B uptake by untreated (live) activated sludge was greater than that of all the treated activated sludge biosorbents over the acidic pH range. The acid treated sludge exhibited the least Remazol Black B biosorption capacity than that of either live or other treated sludges at all the studied pH values. The maximum adsorption at pH 2 was found to be 82.3% with native biomass followed by dried (78.0%), autoclaved (75.4%) and NaOH-treated activated sludge (69.0%). The acid-treated biomass removed only 64.4%. This indicates that all these treatment methods masked the binding sites and physical treatment methods used caused less activity lost when compared to chemical treatment methods used. Since the maximum equilibrium uptakes were observed at pH 2 for all sorbents, all further studies were carried out at pH 2.

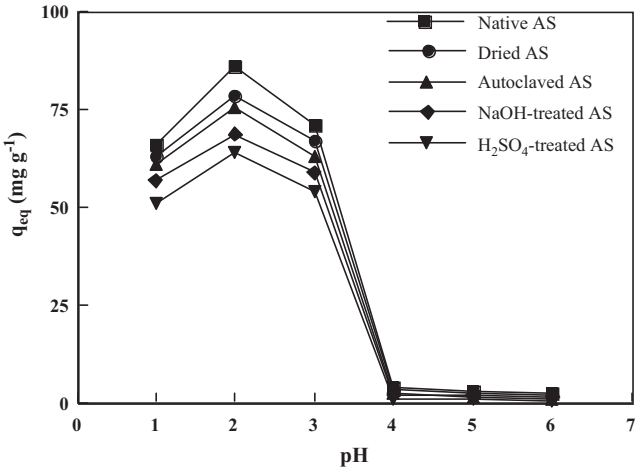

Fig. 2. Effect of initial pH on equilibrium Remazol Black B uptake by untreated and treated activated sludge biosorbents (C_o: 100 mg l^{-1}; T: 25 °C; X: 1 g l^{-1}; agitation rate: 150 rpm).

The medium pH affects the surface charge of the biosorbent, the ionization state of the functional groups on the cell wall and the solubility of dye. The ionic forms of the dye in solution and the surface electrical charge of the biomass, which could be measured in the form of pK_a, zeta potential or isoelectric point, depend on the solution pH. The surface charge on untreated and treated activated sludge biomasses is predominantly negative at pH 3–10 due to the presence of ionized groups such as carboxyl, phosphate and amine groups. However at pH values below the isoelectric point (<3.0) [20], the overall surface charge on cells becomes positive due to protonation of nitrogen-containing functional groups such as amines, which are the major biosorption sites for dye removal. Reactive dyes are known to ionize to a high degree in aqueous solutions to form coloured anions. Four sulfonate groups of Remazol Black B are easily dissociated due to the lower value of pK_a (<1) of the sodium sulfonate groups (i.e., sulfonic groups) attached to the dye molecule so the dye molecule stays under its anionic form at pH higher than 1 [22]. Thus, under acidic conditions, the electrostatic interactions between the anionic dye and the positively charged surface of each sludge biosorbent are maximized due to electrostatic attraction which could be the primary mechanism for the biosorption of dye on each untreated and treated biomass [13–16,20]. Amine groups are also very effective at removing anionic dyes via hydrogen bonding. Vijayaraghavan and Yun [21] confirmed that the amine groups of the bacterium *Corynebacterium glutamicum* were responsible for the binding of reactive dye anions via electrostatic attraction. In contrast, the experimental results indicated that no significant biosorption occurred at pH 6. This may be due to the dominance of other functional groups such as carboxyl, which are negatively charged and exhibit repulsion towards negatively charged Remazol Black B.

3.2. Effect of temperature on Remazol Black B biosorption

Temperature is well known to play an important role in both biosorption rate and equilibrium uptake of dyes by microorganisms. The effect of temperature on the equilibrium dye sorption capacity of each untreated and treated activated sludge biosorbent was investigated in the temperature range of 25–45 °C at varying initial dye concentrations (Tables 1–5). The results revealed that the sorption of Remazol Black B by all activated sludge sorbents

Table 1
Comparison of the second-order kinetic constants, experimental and calculated q_{eq} values and dye removal yields obtained at different initial Remazol Black B concentrations and at different temperatures for live activated sludge.

Temperature (°C)	C_{oRBB} (mg l^{-1})	$q_{eq,exp}$ (mg g^{-1})	Removal %	Second-order kinetic model		
				$k_{2,ad}$ ($\times 10^4$ g mg^{-1} min^{-1})	$q_{eq,cal}$ (mg g^{-1})	R^2
25	24.6	22.0	89.5	163.69	22.0	1.000
	50.9	44.4	87.3	14.36	44.6	0.999
	104.4	86.0	82.3	1.58	87.0	0.999
	255.9	121.4	47.4	0.83	123.5	0.999
	502.5	131.4	26.2	0.70	133.3	0.999
35	25.1	21.1	87.9	157.34	22.1	1.000
	50.8	43.9	86.5	13.21	43.9	0.999
	99.4	75.5	75.9	1.53	76.9	0.999
	248.8	100.6	40.4	0.77	103.1	0.999
	497.3	112.1	22.6	0.67	113.6	0.999
45	25.5	21.1	82.6	150.05	0.962	1.000
	50.8	41.8	82.2	12.05	0.939	0.999
	99.2	74.1	74.7	1.50	0.973	0.999
	249.0	99.0	39.8	0.71	0.978	0.998
	500.2	108.0	21.6	0.63	0.965	0.998

Table 2
Comparison of the second-order kinetic constants, experimental and calculated q_{eq} values and dye removal yields obtained at different initial Remazol Black B concentrations and at different temperatures for heat-treated (dried) activated sludge.

Temperature (°C)	C_{oRBB} (mg l^{-1})	$q_{eq,exp}$ (mg g^{-1})	Removal %	Second-order kinetic model		
				$k_{2,ad}$ ($\times 10^4$ g mg^{-1} min^{-1})	$q_{eq,cal}$ (mg g^{-1})	R^2
25	24.9	21.8	87.7	160.27	21.8	1.000
	49.8	42.8	86.0	14.03	43.1	1.000
	100.6	78.6	78.0	1.58	80.0	0.999
	250.4	111.3	44.5	0.75	113.6	0.999
	497.3	121.7	24.5	0.65	123.5	0.998
35	24.9	21.4	86.0	154.97	21.5	1.000
	50.3	41.2	81.9	13.54	41.5	0.998
	100.4	71.8	71.5	1.42	76.4	0.997
	252.1	106.0	42.1	0.70	108.7	0.998
	500.2	109.3	21.9	0.64	112.4	0.998
45	24.7	19.7	79.7	150.04	19.7	1.000
	50.3	36.1	71.8	12.22	36.2	1.000
	100.2	69.2	69.1	1.34	70.4	0.999
	247.7	89.8	36.3	0.68	92.66	0.999
	503.6	103.8	20.6	0.62	106.4	0.998

indicated an exothermic character and equilibrium dye uptake diminished with temperature rising. Since sorption is an exothermic process, this is an expected result due to weakened physical bonding between the dye and active sites of these biosorbents with increasing temperature. Overall, it is obvious that the biosorption capacity of native activated sludge for the dye at 25 °C was the highest when compared to maximum dye adsorptions by treated biomasses. Data also indicated that the effect of temperature at

Table 3
Comparison of the second-order kinetic constants, experimental and calculated q_{eq} values and dye removal yields obtained at different initial Remazol Black B concentrations and at different temperatures for autoclaved activated sludge.

Temperature (°C)	C_{oRBB} (mg l^{-1})	$q_{eq,exp}$ (mg g^{-1})	Removal %	Second-order kinetic model		
				$k_{2,ad}$ ($\times 10^4$ g mg^{-1} min^{-1})	$q_{eq,cal}$ (mg g^{-1})	R^2
25	25.2	21.7	86.1	154.67	21.7	1.000
	50.9	42.9	84.3	12.49	43.1	1.000
	100.0	75.4	75.4	1.42	76.9	0.998
	252.3	111.1	44.0	0.65	115.0	0.997
	503.1	121.1	24.1	0.61	123.5	0.999
35	25.0	21.0	84.1	141.22	21.0	1.000
	50.9	40.8	80.0	11.12	41.0	0.999
	100.5	72.6	72.3	1.33	74.1	0.999
	247.9	97.0	39.1	0.59	100.0	0.999
	499.6	106.1	21.3	0.60	108.7	0.999
45	24.8	19.6	79.0	136.89	19.6	1.000
	50.2	35.4	70.5	10.02	35.6	0.999
	101.0	63.2	62.5	1.28	64.5	0.998
	249.6	81.4	32.6	0.60	84.0	0.998
	500.2	99.7	19.9	0.56	102.1	0.997

Table 4
Comparison of the second-order kinetic constants, experimental and calculated q_{eq} values and dye removal yields obtained at different initial Remazol Black B concentrations and at different temperatures for acid-washed activated sludge.

Temperature (°C)	C_{oRBB} (mg l^{-1})	$q_{eq,exp}$ (mg g^{-1})	Removal %	Second-order kinetic model		
				$k_{2,ad}$ ($\times 10^4$ g mg^{-1} min^{-1})	$q_{eq,cal}$ (mg g^{-1})	R^2
25	24.8	17.7	71.4	117.81	17.7	1.000
	50.5	34.6	68.4	9.04	34.8	0.999
	99.2	63.9	64.4	1.14	64.4	0.998
	250.1	91.7	36.6	0.53	93.2	0.997
	500.7	102.8	20.5	0.50	104.4	0.997
35	24.8	16.7	67.1	96.43	16.7	0.999
	50.3	32.7	64.9	8.01	32.9	0.999
	99.8	60.1	60.2	1.06	61.7	0.998
	250.4	89.2	35.6	0.50	92.6	0.997
	500.2	95.8	19.2	0.47	97.7	0.997
45	24.8	15.7	63.1	79.56	15.8	1.000
	50.1	30.9	61.7	7.32	31.0	0.999
	101.0	57.6	57.1	0.94	59.2	0.999
	251.2	70.9	28.2	0.48	72.1	0.994
	500.2	83.7	16.7	0.44	85.9	0.995

higher initial dye concentrations on the biosorption capacity of each biomass was more impressive than that of lower initial dye concentrations. It was observed that 86.0, 78.6, 75.4, 63.9 and 68.7 mg dye per gram of untreated (live) and treated (dried, autoclaved, acid- and base-treated) activated sludges were adsorbed at equilibrium at 25 °C and at the initial dye concentration of 100 mg l^{-1}, respectively. With raising the temperature to 45 °C, biosorption capacity of live and treated (dried, autoclaved, acid- and base-treated) biomass dropped to 74.1, 69.2, 63.2, 57.6 and 59.9 mg g^{-1} showing 13.8%, 12.0%, 16.2%, 9.9% and 12.8% reduction in uptake capacity of each biosorbent, respectively.

3.3. Effect of initial Remazol Black B concentration on Remazol Black B biosorption

A higher initial dye concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases, thus increases the uptake. In addition, increasing initial dye concentration increases the number of collisions between dye anions and biosorbent, which enhances the sorption process. The effect of initial dye concentration on the dye sorption capacity and yield of each biosorbent was investigated between 25 and 500 mg l^{-1} at the optimum initial pH value of 2 and at three different temperatures and the results are tabulated in Tables 1–5. Different binding capacities and yields depending on the treatment method, initial dye concentration and temperature were observed. At all temperatures studied uptake of the dye by each sorbent enhanced notably with increasing initial dye concentration tending to saturation at higher dye concentrations. At 25 °C with changing initial dye concentration from approximately 25 to 500 mg l^{-1}, the dye amount sorbed increased from 22.0 to 131.4 mg g^{-1} for live sludge, 21.8–121.7 mg g^{-1} for heat-treated (dried) sludge, 21.7–121.1 mg g^{-1} for autoclaved sludge, 17.7–102.8 mg g^{-1} for acid-treated sludge, 20.0–118.9 mg g^{-1} for base-treated biomass. The removal yields determined at different Remazol Black B concentrations and temperatures for each untreated and treated activated sludge biomass were also compared in Tables 1–5. At all temperatures studied, percent dye removal was higher at low dye concentrations for all biosorbents due to availability of unoccupied binding sites on the sorbents. Percent dye removal diminished with increasing dye concentration because of nearly complete coverage of the binding sites of each biosorbent at high dye concentrations. The results also indicated that among the five biosorbents, native sludge showed the highest equilibrium capacity for Remazol Black B at all concentrations and temperatures tested.

Table 5
Comparison of the second-order kinetic constants, experimental and calculated q_{eq} values and dye removal yields obtained at different initial Remazol Black B concentrations and at different temperatures for NaOH-treated activated sludge.

Temperature (°C)	C_{oRBB} (mg l^{-1})	$q_{eq,exp}$ (mg g^{-1})	Removal %	Second-order kinetic model		
				$k_{2,ad}$ ($\times 10^4$ g mg^{-1} min^{-1})	$q_{eq,cal}$ (mg g^{-1})	R^2
25	24.9	20.0	80.3	145.92	20.3	1.000
	50.3	40.3	80.1	10.35	40.6	0.999
	99.5	68.7	69.0	1.39	69.9	0.999
	249.3	103.0	41.3	0.63	105.5	0.998
	506.0	118.9	23.5	0.59	121.9	0.999
35	24.7	18.8	76.0	135.54	18.9	1.000
	50.4	38.0	75.3	10.21	38.3	0.999
	99.4	67.6	68.0	1.26	68.8	0.999
	248.5	93.3	37.6	0.59	94.6	0.998
	503.6	103.8	20.6	0.57	105.1	0.997
45	25.0	17.0	68.0	130.77	17.0	1.000
	49.7	32.3	64.9	9.56	32.4	1.000
	100.5	59.9	59.5	1.22	61.4	0.999
	251.0	72.5	28.9	0.58	73.9	0.998
	501.3	90.6	18.1	0.52	92.8	0.998

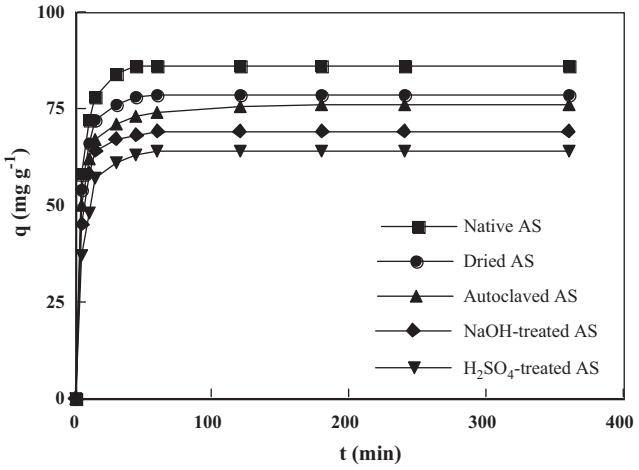

Fig. 3. Biosorption curves obtained in Remazol Black B adsorption onto untreated and treated activated sludge biosorbents at 100 mg l^{-1} initial dye concentration (initial pH: 2; *T*: 25 °C; *X*: 1 g l^{-1}; agitation rate: 150 rpm).

3.4. Biosorption behaviours

Kinetics of sorption describing the pollutant uptake rate is one of the important characteristics defining the efficiency of sorption and feasibility of adsorbent for its use in water pollution control. Hence, the kinetics of Remazol Black B dye removal has been carried out to understand the dye adsorption behaviour of the five activated sludge sorbents. For this purpose, dye uptake (q) was plotted against the time for each biosorbent at a representative initial dye concentration of 100 mg l^{-1} and at the temperature of 25 °C (Fig. 3). The time profiles of dye uptake were single, smooth and continuous similar curves leading to saturation, suggesting the possible monolayer coverage of dye on the surface of each biosorbent. Although the adsorption studies were carried out for 24 h in order to determine the effect of time on sorption, the data in Fig. 3 indicated that the time required to reach equilibrium for sorption appears to be much more shorter for each sorbent. The first 2 h of adsorption was sufficient to reach equilibrium for each biomass. Although each biomass showed an appreciable sorption of dye, the rate of dye uptake and the amount of adsorbed dye changed with respect to treatment method and time. It is clear that the biosorption rate and capacity of live activated sludge was higher than that of other treated biosorbents. For all the biosorbent types initial sorption of dye occurred rapidly and the majority of dye uptake took place within the first 30 min of contact. Such a rapid and higher uptake of Remazol Black B dye in all cases indicates that all sorbents have an affinity for the dye anions pointing towards physical adsorption and that the uptake of dye occurs predominantly by surface binding – sorption kinetics – and that available sites on the sorbents are the limiting factor for the sorption. Moreover, according to the literature, if equilibrium is achieved within 3 h, the process is usually kinetic controlled and above 24 h, it is diffusion controlled [23]. Thus, the adsorption equilibrium time for each biosorbent suggests that adsorption kinetics affects the overall adsorption kinetics. It is evident that live activated sludge biomass is the most effective biosorbent for the removal of Remazol Black B although comparable removals are achieved by dried, autoclaved, acid-treated and base-treated activated sludge biomasses under the same conditions.

Carboxyl, amine, phosphonate, sulfonate and hydroxyl groups on the surfaces of biomasses have been well established as being responsible for dye binding [10,20]. It is thought that if the number of these groups is low, most biosorbents show low sorption capacities, and uptake capacities may be enhanced via several physical/chemical treatment methods. The enhanced sorption capacity was attributed to the eliminating impurities and ions blocking the binding sites, and exposing additional binding sites or to more complex actions taking place on the cell surface, such as the formation of electrostatic bonds, change in the overall surface charge and modification of binding sites [6,8–10,17–19]. Common chemical pre-treatments included acid, alkaline, ethanol, salt and acetone treatments of the biomass. Vijayaraghavan and Yun [21] employed several chemical agents (mineral acids, NaOH, Na_2CO_3, $CaCl_2$ and NaCl) for the pre-treatment of *C. glutamicum* in the biosorption of Reactive Black 5. The authors identified that the treatment of biomass with 0.1 M HNO_3 is the most suitable for opening new binding sites, and this method enhanced Reactive Black 5 uptake capacity by 1.3 times as that of the raw biomass. Bayramoğlu et al. [9] found 81.1 and 132.5 mg g^{-1} Reactive Blue 4 uptake capacities for native and acid-treated dry fungal preparations, respectively, at 600 mg l^{-1} initial dye concentration. Fu and Viraraghavan [24] used the chemically pretreated *Aspergillus niger* for the biosorption of reactive dye Congo Red. They indicated that HCl, H_2SO_4, $CaCl_2$, $NaHCO_3$, and NaCl pre-treatments all increased the biosorption capacity. Patel and Suresh [25] employed with the isolated fungus *Aspergillus foetidus* for the removal of 100 mg l^{-1} of Reactive Black 5 dye at acidic pH (2–3). They indicated that the pre-treatment of fungal biomass witth 0.1 M NaOH enhanced the uptake of dye as compared to untreated fungal biomass. Common physical pre-treatments contained mainly drying and autoclaving of the biomass. Bayramoğlu and Arica [26] observed that the biosorption capacity of *Trametes versicolor* for Direct Blue 1 (at 800 mg l^{-1} initial concentration) increased from 101.1 to 152.3 mg g^{-1} after heat treatment. They suggested that the native form of the fungal biomass is hydrophobic in nature. Most of these hydrophobic entities get removed due to heat-treatment thus changing the surface properties and leading to changes in contact angles and biosorption capacity. Fu and Viraraghavan [24] explored that autoclaving increased the Congo Red biosorption capacity of living *A. niger* from 12.1 to 13.5 mg g^{-1}. They suggested that the autoclaving process could result in disruption and thus expose latent sites, consequently increasing the dye adsorption. Although many studies showed that a lot of physical/chemical treatment methods improved the biosorption performance, however, some studies indicated that similar pre-treatment methods affected the biosorption capacity negatively. Why the pre-treatment adversely affected the loading capacity of the biomass was tried to be explained by the masking effect of treatment method on the reactive sites, by denaturation of active sites and/or by unfavourable reactions occurred between chemical agents and active sites [8,10,21,24–26]. Fu and Viraraghavan [24] observed that NaOH treatment decreased the biosorption capacity of *A. niger* for Congo Red. This was explained by saying that pre-treatment by NaOH could generate anionic sites on the surface of fungal biomass and thus increase repulsion between the negatively charged surface of the fungal biomass and the colored anions of Congo Red. It can be concluded that the effective pre-treatment is related to method, biomass type and dye molecule and is unpredictable.

The experimental results showed that the use of live activated sludge directly gave the maximum Remazol Black B uptake. In general all the physical and chemical pre-treatments used to kill the activated sludge decreased the Remazol Black B biosorption capacity of the biomass. The biosorption of Remazol Black B ions onto acid-treated activated sludge appeared to be the lowest when compared to the biosorption of dye onto other live and treated sludges at equilibrium. At 25 °C for 100 mg l^{-1} initial dye concentration, the decreases in the biosorption capacities of the dried and autoclaved activated sludges (physically treated biomasses) were about 1.09- and 1.15-fold, respectively, whereas the reductions in the biosorption capacities of the acid-treated and base-treated activated sludges (chemically treated biomasses) were about 1.35- and

1.25-fold, respectively, compared to the native form. Compared with chemical pre-treatments, physical pre-treatments decreased the biosorption capacity of native biomass by a relatively low extent. Why the physical pre-treatments reduced the dye uptake can be explained that cells when subjected to heat treatment or autoclaving can suffer rupture and denaturation of proteins on the cell wall, decreasing the cell wall binding sites thereby decreasing the possibility of dye biosorption. As the acid treatment causes degradation of acid labile cell wall components into oligomers (i.e., polysaccharides and proteins), the acid treatment was also found inefficient in increasing the biosorption capacity of the activated sludge biomass. Moreover, the base-treated biomass had also a low biosorption capacity for the Remazol Black B dye. The base treatment causes hydrolysis of the phospholipids portion of the cell membrane, thus a decrease in availability of the phosphate groups for binding with the dye molecule due to the disintegration of the cell membranes. Moreover pre-treatment by NaOH could generate anionic sites on the cell surface, which cause repulsion between the negatively charged surface and the coloured anions of Remazol Black B [10,20,24].

3.5. Kinetic modelling of Remazol Black B biosorption

Adsorption is a time-dependent process. In the removal of dyes from wastewater, it is necessary to know the rate of adsorption for process design, operation control and adsorbent evaluation. For this purpose simplified pseudo-second-order kinetic model was tested to fit the experimental data. This model is the most commonly used to describe the sorption of dyes and basically include all steps of adsorption such as external film diffusion, adsorption, and internal particle diffusion, so it is a pseudo-model as pointed out by Ho and McKay [23]. Contrary to other well-established kinetic models, pseudo-second-order model also predicts the adsorption behaviour over the whole range of adsorption period. Another advantage of using this model is that there is no need to know the equilibrium uptake capacity from the experiments, as it can be calculated from the model. The pseudo-second-order equation is based on the sorption capacity of the solid phase and is expressed as:

$$\frac{dq}{dt} = k_{2,ad}(q_{eq} - q)^2 \tag{2}$$

where $k_{2,ad}$ is the rate constant of second-order biosorption of Remazol Black B. After integration and applying the boundary conditions of $t = 0$ to $t = t$ and $q = 0$ to $q = q_{eq}$; the integrated form of Eq. (2) becomes a linear function and model parameters of q_{eq} and $k_{2,ad}$ can be estimated from the slope and intercept of the t/q against t plot.

The rate constants ($k_{2,ad}$) and equilibrium uptake values (q_{eq}) were determined from the slope and intercept of t/q versus t plots (data not shown) for each case. The values of the parameters $k_{2,ad}$ and q_{eq} and of correlation coefficients are also presented in Tables 1–5 for each dye–biosorbent system. The results indicated that second-order rate constants were also affected by the treatment method, initial dye concentration and temperature. For all biosorbents, the pseudo-second-order rate constant diminished notably with the initial dye concentration and the values of q_{eq} increased with increasing concentration of dye presumably due to the enhanced mass transfer of dye molecules to the surface of each biomass. Tables 1–5 show that the rate constants were also affected by changing the temperature for each biosorbent. For all sorbents with raising the temperature from 25 to 45 °C, the rate constants of pseudo-second-order model showed a decline, which may be attributed to dominant surface adsorption. The rate constants of live activated sludge appeared to be the highest compared to the rate constants of other biosorbents. The correlation coefficients obtained greater than 0.994 and the adequate fitting of theoretical and experimental q_{eq} values for all cases suggest the applicability of second-order kinetic model based on the assumption that the rate limiting step may be the chemisorption in explaining the kinetics of biosorption for the entire sorption period for the five biosorbents. The parameters of these kinetic modelling can be used for a reactor design.

3.6. Equilibrium modelling of Remazol Black B biosorption

In order to discover the sorption capacity of the five activated sludge biosorbents for Remazol Black B dye, the experimental data points were fitted to the Langmuir and Freundlich (two-parameter models), Redlich–Peterson and Langmuir–Freundlich (Sips) (three-parameter models) empirical models, which are the most frequently used equations in the literature describing the non-linear equilibrium between adsorbed dye on the cells (q_{eq}) and dye in solution (C_{eq}) at a constant temperature.

The Langmuir equation, which is valid for monolayer sorption on to a surface a finite number of identical sites and has been used extensively for dilute solutions in the following form.

$$q_{eq} = \frac{Q^o b C_{eq}}{1 + bC_{eq}} \tag{3}$$

where Q^o is the maximum amount of the dye ion per unit weight of biomass to form a complete monolayer on the surface bound at high C_{eq}, and b is a constant related to the affinity of the binding sites [27].

The Freundlich expression is an empirical equation based on the sorption onto a heterogeneous surface. The Freundlich equation generates an exponential shaped theoretical equilibrium curve and is represented as:

$$q_{eq} = K_F C_{eq}^{1/n} \tag{4}$$

where K_F and n are the Freundlich constants characteristic of the system [28].

The further three-parameter empirical Redlich–Peterson model is widely used as a compromise between Langmuir and Freundlich systems. It has a linear dependence on concentration in the numerator and has an exponential dependence on concentration in the denominator. The non-linear form of the model is given by Eq. (5):

$$q_{eq} = \frac{K_{RP} C_{eq}}{1 + a_{RP} C_{eq}^{\beta}} \tag{5}$$

where K_{RP}, a_{RP} and β are the Redlich–Peterson parameters. The exponent β lies between 0 and 1. According to this equation, equilibrium curve follows Henry's law for $\beta = 0$ and follows Langmuir isotherm equation for $\beta = 1$ [29].

Langmuir–Freundlich model is another three-parameter empirical model for the representing equilibrium sorption data. It can be considered as a combination of Langmuir and Freundlich equations. This model suggests that the equilibrium data follow Freundlich isotherm at low solute concentrations and thus do not obey Henry's law, and follow Langmuir pattern at higher solute concentrations (Eq. (6)):

$$q_{eq} \frac{A C_{eq}^m}{1 + B C_{eq}^m} \tag{6}$$

where A, B and m are the Langmuir–Freundlich parameters. Values for m (the heterogeneity factor) $\gg 1$ indicate heterogeneous adsorbents, while values closer to or even 1.0 indicate a material with relatively homogenous binding sites. In this case the model is reduced to the Langmuir equation.

The experimental equilibrium data of Remazol Black B biosorption by all the untreated and treated activated sludge biomasses

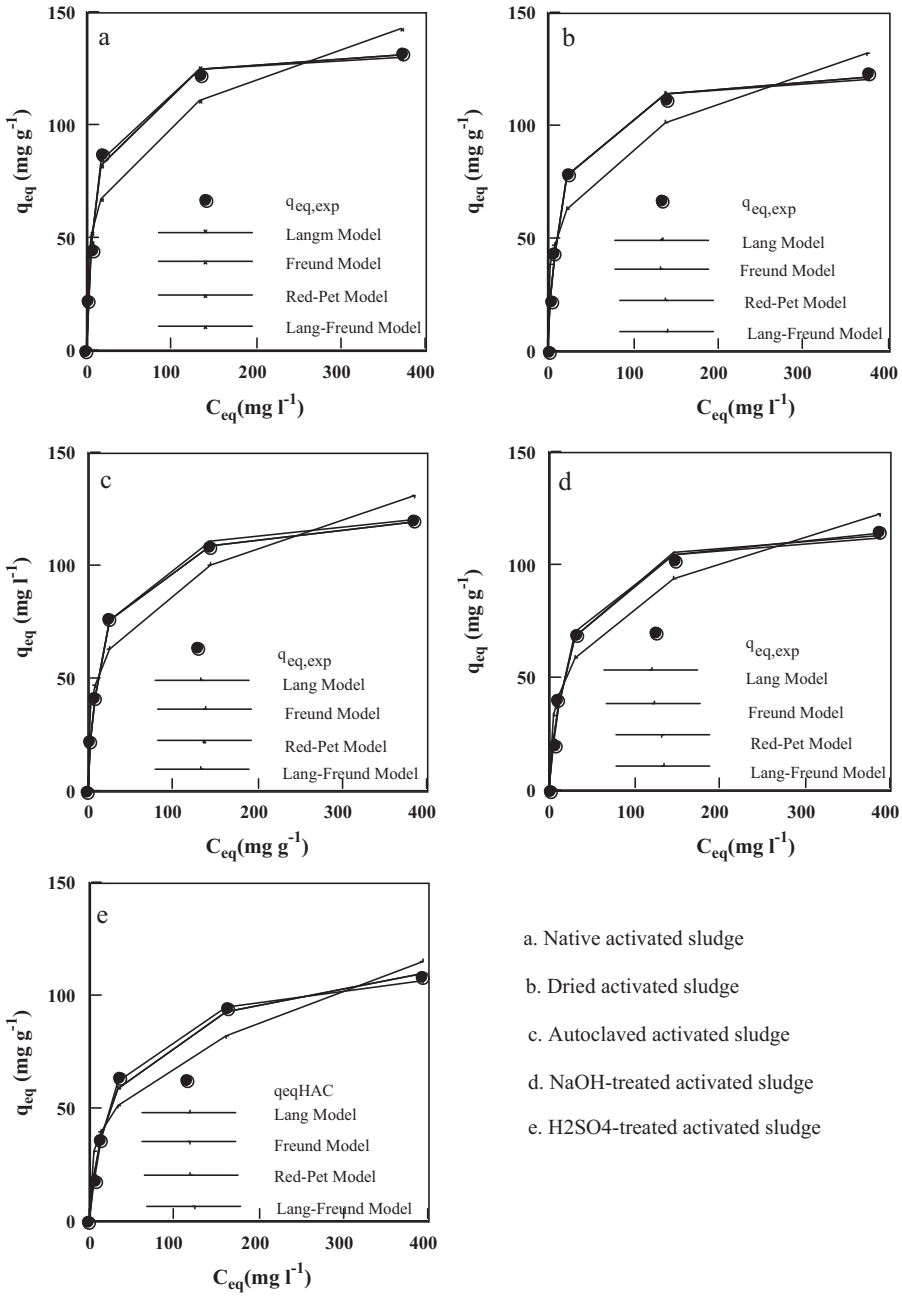

Fig. 4. Comparison between the experimental equilibrium data of Remazol Black B biosorption (points) and model predictions (curves) obtained at 25 °C (initial pH: 2; *T*: 25 °C; *X*: 1 g l^{-1}; agitation rate: 150 rpm).

obtained at 25 °C were given in Fig. 4. All the isotherms are positive, regular and concave to the concentration axis (L-type isotherm) indicating an affinity for sorption. The isotherm curves of live, dried, autoclaved and base-treated activated sludge biomasses indicated a limiting sorption capacity attained at equilibrium concentration of about 350–400 mg l^{-1}. The acid-treated biosorbent exhibited an unsaturation behaviour over the concentration range involved. However all cases exhibited a complete monolayer of dye covering the surface of each biosorbent.

The relative model parameters were estimated by nonlinear regression analysis at different temperatures and are tabulated in Tables 6–9 with the average percentage errors. The magnitude of average percentage errors was the criteria for the selection of the most suitable isotherm model. The average percentage error was calculated using Eq. (7). In Eq. (7), the subscripts 'exp' and 'calc' show the experimental and calculated values and *N* is the number of measurements:

$$\varepsilon = \frac{\sum_{i=1}^{N} |(q_{eq,i\,\mathrm{exp}} - q_{eq,i,\mathrm{calc}})/q_{eq,i,\mathrm{exp}}|}{N} \times 100 \quad (7)$$

In view of the values of average percentage errors in the tables, the Langmuir–Freundlich model exhibited the best fit to the biosorption data of each dye–biosorbent system in the concentration and temperature ranges studied. Moreover, the Langmuir-model also seemed to agree well with the entire data set considering that obtained percentage error values were lower than 8.31% in all cases when compared to largely deviated Freundlich model ($\varepsilon\% > 15.96$). Using the model parameters, equilibrium uptake values of Remazol Black B dye for each untreated and treated biomass were predicted from the related formulae at all temperature values studied. The comparison of the experimental and predicted equilibrium uptake (q_{eq}) values of dye obtained at

Table 6
Freundlich model parameters estimated for Remazol Black B biosorption onto untreated and treated activated sludge biomasses at different temperatures.

	Temperature (°C)	KF [(mg g^{-1}) (mg l^{-1})$^{-1/n}$]	n	ε %
Live activated sludge	25	32.0	3.98	27.96
	35	28.5	3.97	20.53
	45	25.8	3.96	24.53
Dried activated sludge	25	28.5	3.90	24.09
	35	25.5	3.86	22.32
	45	20.1	3.53	22.99
Autoclaved activated sludge	25	26.6	3.75	23.01
	35	24.7	3.64	22.62
	45	17.5	3.37	15.96
H_2SO_4-treated activated sludge	25	16.5	3.16	25.23
	35	14.8	3.09	26.54
	45	13.7	3.01	23.43
NaOH-treated activated sludge	25	20.93	3.31	20.44
	35	18.12	3.26	24.60
	45	14.70	3.12	19.89

Table 7
Langmuir model parameters estimated for Remazol Black B biosorption onto untreated and treated activated sludge biomasses at different temperatures.

	Temperature (°C)	Q^o (mg g^{-1})	b ($\times 10^2$ l mg^{-1})	e%
Live activated sludge	25	134.8	8.8	4.48
	35	122.2	8.0	3.50
	45	111.5	6.6	5.09
Dried activated sludge	25	126.5	7.4	2.24
	35	114.4	6.0	2.21
	45	103.5	4.4	5.50
Autoclaved activated sludge	25	123.1	6.2	1.74
	35	109.6	5.8	3.07
	45	101.0	3.9	4.75
H_2SO_4-treated activated sludge	25	113.2	3.1	6.75
	35	100.7	2.8	7.58
	45	88.5	2.4	7.44
NaOH-treated activated sludge	25	118.2	4.3	4.46
	35	105.3	4.1	6.02
	45	94.8	3.3	8.31

Table 8
Redlich–Peterson model parameters estimated for Remazol Black B biosorption onto untreated and treated activated sludge biomasses at different temperatures.

	Temperature (°C)	K_{RP} (l g^{-1})	a_{RP} ($\times 10^2$ l^b mg^{-b})	β	ε %
Live activated sludge	25	11.2	8.9	1.000	4.47
	35	10.8	8.3	0.974	4.02
	45	7.9	6.6	1.000	6.09
Dried activated sludge	25	9.5	8.1	0.989	2.42
	35	7.0	7.4	1.000	2.21
	45	5.8	6.4	1.000	6.50
Autoclaved activated sludge	25	8.2	7.1	0.988	1.88
	35	6.8	6.2	1.000	3.07
	45	5.2	6.1	0.978	4.64
H_2SO_4-treated activated sludge	25	3.5	3.8	1.000	6.75
	35	3.0	3.3	1.000	7.58
	45	2.8	2.5	1.000	10.44
NaOH-treated activated sludge	25	6.2	6.1	0.988	4.41
	35	4.8	5.3	1.000	6.02
	45	3.4	4.4	0.964	9.97

Table 9
Langmuir–Freundlich model parameters estimated for Remazol Black B biosorption onto untreated and treated activated sludge biomasses at different temperatures.

	Temperature	A (l^m mg^{1-m} g^{-1})	B (l mg^{-1})^m	m	ε%
Live activated sludge	25	11.54	7.9	1.23	2.81
	35	10.69	6.9	1.14	4.03
	45	4.43	4.1	0.95	2.54
Dried activated sludge	25	8.84	7.1	1.02	1.88
	35	7.43	6.4	0.98	1.72
	45	3.40	3.3	1.13	3.32
Autoclaved activated sludge	25	8.09	6.4	0.99	1.90
	35	5.60	5.2	1.09	2.61
	45	6.08	5.6	0.84	4.08
H_2SO_4-treated activated sludge	25	1.78	1.7	1.24	3.43
	35	1.20	1.2	1.3	2.06
	45	0.85	1.0	1.40	4.64
NaOH-treated activated sludge	25	6.78	5.2	0.89	5.24
	35	2.84	2.7	1.20	2.38
	45	1.92	2.1	1.17	4.64

25 °C is also presented in Fig. 4. The data in Fig. 4 also confirmed that the Langmuir–Freundlich and Langmuir models closely predicted the equilibrium data, as evident from the overlapping of their model curves. The suitability of Langmuir–Freundlich model shows that all biosorbents represented some heterogeneity.

K_F, one of the Freundlich constants has been used as a relative measure of adsorption capacity (K_F reaches the value of q_{eq} when the equilibrium concentration C_{eq} approaches to unity, thus can be considered as an indicative parameter of the adsorption strength). A greater value of K_F indicates a higher capacity for adsorption. From Table 6, all measured values of K_F showed easy uptake of the dye with high adsorptive capacity of each biosorbent and significant differences in sorption capacities among these sorbents with respect to temperature. The highest value of K_F was determined to be 32.0 for live activated sludge at 25 °C. As expected the value of K_F for the adsorption of Remazol Black B dye on native activated sludge is significantly higher than that of adsorption on other biosorbents. The K_F value found for acid-treated sludge also showed the lowest adsorptive capacity of this biomass. The n, the other Freundlich constant, is an empirical parameter that varies with the degree of heterogeneity indicating the degree of nonlinearity between dye uptake capacity and unadsorbed dye concentration and is related to the distribution of bonded ions on the sorbent surface. In general $n > 1$ illustrates that adsorbate is favourably adsorbed on an adsorbent, corresponds to a normal an L-type Langmuir isotherm, and the higher the n value the stronger the adsorption intensity. Table 6 also indicated that n is greater than unity, indicating that Remazol Black B dye is favourably adsorbed by all the sorbents at all the temperatures studied.

Langmuir model serves to estimate the maximum uptake or the total capacity of biosorbent for the dye (Q^o) where it could not be reached in the experiments. Values of Q^o and b calculated from the Langmuir model at different temperatures are tabulated in Table 7. The Langmuir model parameters were also largely dependent on the treatment method and temperature. All the values of Q^o appeared to be significantly higher for the dye-live activated sludge system in comparison with the maximum dye uptakes on the other activated sludge biomasses, indicated that the resting cells have the maximum capacity at all temperatures studied. The other Langmuir constant b is related to the free energy change of adsorption, and indicates the affinity of sorbent for the binding of dye. Its value is the reciprocal of the dye concentration at which half of the saturation of the adsorbent is attained (or Remazol Black B amount of $Q^o/2$ is bound) so a high value of b, indicates a steep desirable beginning of the isotherm which reflects the high affinity of the sorbent for the

sorbate resulting in a stable adsorption product. The higher values of b obtained for live activated sludge–dye system implied strong bonding of dye to this biosorbent.

Related Redlich–Peterson adsorption parameters calculated according to the three-parameter Redlich–Peterson isotherm model were listed in Table 8 for each biosorbent at three different temperatures. The model parameter K_{RP} also indicated that the relative biosorption capacity of each sludge biosorbent increased with decreasing temperature and reached to maximum at 25 °C. The values of K_{RP} and a_{RP} also indicated that the adsorption capacity of un-treated biomass is significantly higher than that of other activated sludge biosorbents. It should be noted that β normally lying between 0 and 1, indicated a favourable adsorption of dye onto each activated sludge biosorbent. From Table 8, it is worth noting that the β values were close to unity for all cases, i.e., the isotherms approach the Langmuir form.

The corresponding Langmuir–Freundlich parameters of A, B and m for different temperatures along with the percentage errors are given in Table 9 for each dye–sorbent system. Langmuir–Freundlich constant A, also indicates a relative measure of adsorption capacity and affinity of each biosorbent to Remazol Black B dye, was found maximum at 25 °C for un-treated activated sludge. Similar to Redlich–Peterson model, the values of Langmuir–Freundlich model exponent m were also close to unity for all cases studied (almost homogeneous sorbents).

Although the equilibrium model constants have different meanings, such as Q^o is the monolayer adsorption capacity while K_F is the relative adsorption capacity or adsorption power, etc., all of them led to the same conclusion about the correlation of the experimental data: as indicated in Tables 6–9, live activated sludge showed the highest adsorption capacity for Remazol Black B dye, and the adsorption capacity of each biomass for the dye decreased with increasing temperature.

4. Conclusion

In recent years some physical and chemical pre-treatment methods have been proposed to increase the biosorption capacity of the biomass for dye ions. Many studies indicated that these methods improved the biosorption performance, however, other studies indicated that similar pre-treatment methods affected the biosorption capacity negatively. The biosorption characteristics of the live and treated activated sludge biomasses for the removal of Remazol Black B ions showed that the level of Remazol Black B uptake was dependent on treatment method, solution pH, temperature, and initial Remazol Black B concentration. All the treatment methods diminished the dye biosorption capacity of activated sludge as compared to the untreated biomass. The maximum sorption capacity determined according to the Langmuir model at an initial pH value of 2 and at 25 °C, in decreasing order, was as follows: live activated sludge (134.8 mg g^{-1})> dried activated sludge (126.5 mg g^{-1})> autoclaved activated sludge (123.1 mg g^{-1})> NaOH-treated activated sludge (118.2 mg g^{-1})> H_2SO_4-treated activated sludge (113.2 mg g^{-1}). The different Remazol Black B binding capacities of the five resting and treated activated sludge cells investigated in this study may be attributable to their surface properties.

While using the pre-treated biomass on a large scale the cost raise due to pre-treatment should be taken into account. In the case of activated sludge biomass, as the resting cells had the maximum biosorption efficiency and as no pre-treatment was needed, live biomass could be used effectively for the removal of Remazol Black B.

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