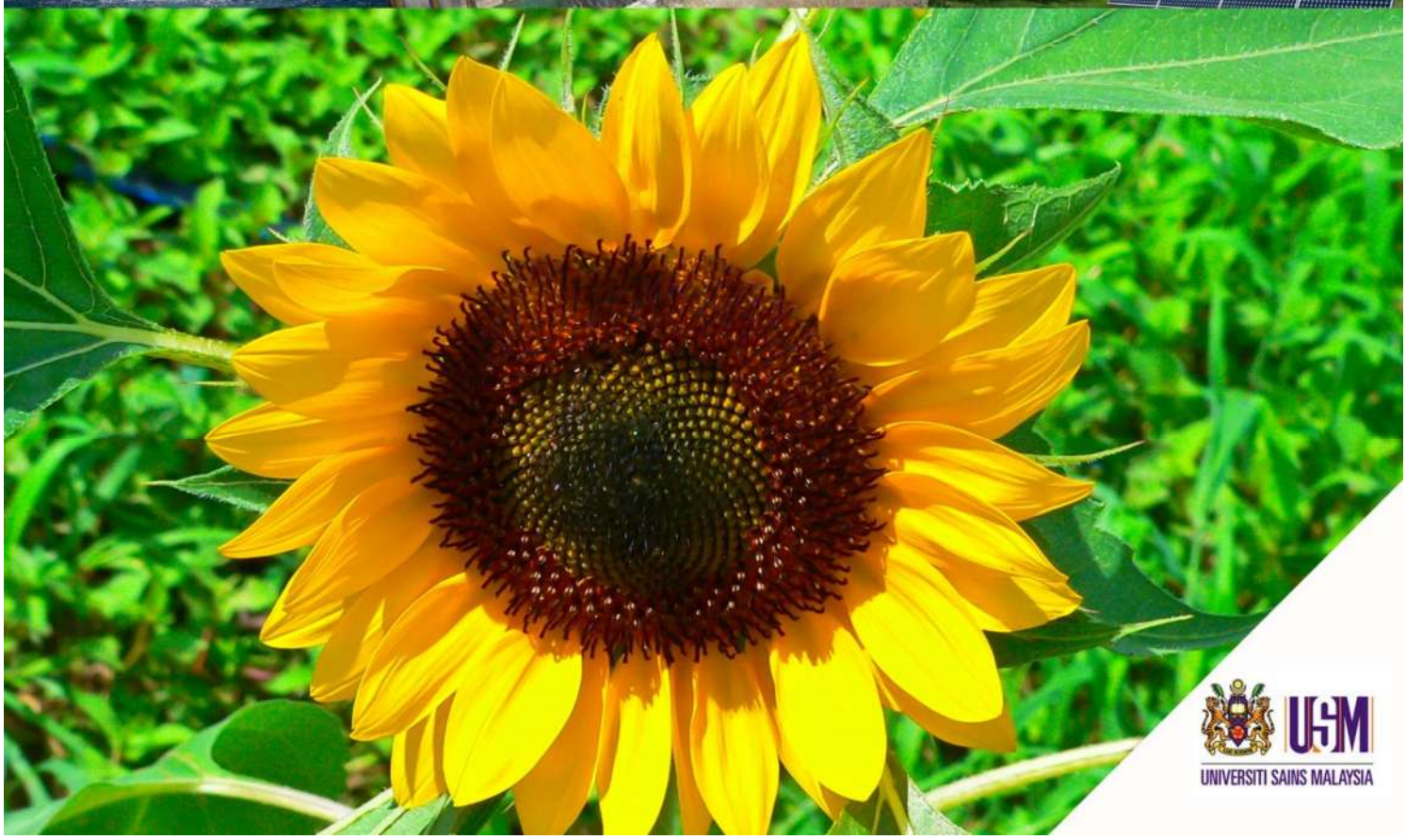
INTERNATIONAL CONFERENCE ON ENVIRONMENT 2012

GREEN TECHNOLOGY for Sustainable Tomorrow

11-13 December 2012
Parkroyal Hotel, Penang
MALAYSIA



USM
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FOREWORD FROM THE VICE CHANCELLOR

Assalamualaikum and greetings,

On behalf of Universiti Sains Malaysia (USM), I would like to extend a warm welcome to all delegates of the 6th International Conference on Environment 2012 (ICENV 2012) organised by the School of Chemical Engineering, USM. As the world population grows and higher standards of living are expected, there will be increasing stress on the world's limited resources. Creating a sustainable world that provides a safe, healthy and sustainable life for all people should be a priority for the engineering profession. In facing these challenges, we require a unique and innovative way of thinking, taking actions and setting goals other than the norm.

I am very pleased that ICENV 2012 has selected "Green Technologies for Sustainable Tomorrow" as the theme of the conference. This is in line with the University's vision in empowering the society and leads them towards sustainable development in ascertaining a more lasting future and survival of the planet. ICENV 2012 will be the perfect venue for delegates from different parts of the world to come together and deliberate issues on the emerging green technologies for the purpose of shaping a sustainable future and disseminate their new research findings in the fields of environment. I hope that this conference will provide educational and professional values in the pursuit of sustainable development, conservation and restoration of resources to enhance the health of humanity and our environment.

My heartfelt appreciation and congratulations to the School of Chemical Engineering for the excellent effort in organising this conference. I wish all the success to the ICENV 2012 and that all presenters and participants will gain tremendous knowledge and experience from it.

Thank you.

Professor Dato' Omar Osman
Vice Chancellor
Universiti Sains Malaysia

FOREWORD FROM THE CONFERENCE CHAIRMAN

It gives me great pleasure to welcome all of you to the 6th International Conference on Environment 2012 (ICENV 2012). We are all facing daunting problems of sustainable development where the environment continuous to deteriorate and some natural resources approaches critical point. These problems are the major threat for us to preserve and enhance the health of humanity and our environment.

The conference's theme - "Green Technologies for Sustainable Tomorrow" is clearly an important and crucial topic on environment focusing on green and sustainable development for sustainable future. The main objective of this conference is to integrate green innovation and technologies from research-commercial settings into sustainable development so as to build a sustainable environment for the future generation. I hope that ICENV 2012 will be the appropriate platform to imbue and strengthen participants with the need to embrace ecological protection, conservation of resources and human development based on the virtues of equity, accessibility, availability, affordability and appropriateness, in line with the vision of USM, which is 'Transforming Higher Education for a Sustainable Tomorrow'.

On behalf of the organizing committee, I would like to thank the participants, speakers, committee members and sponsors for their contributions. The conference could not be successful without your participation and dedication, commitment and valuable time of all the committee members and many of the student volunteers, who plays a pivotal role behind the organization and contributes towards the success of the conference. Finally, I sincerely hope that your participation in this conference is a rewarding experience that you have an opportunity to meet other researches for future networking and collaboration. I also wish that all participants will enjoy the cultural and natural beauty of Penang, The Pearl of the Orient.

Thank you.

Azlina Harun @ Kamaruddin
Professor
Universiti Sains Malaysia

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CONFERENCE PROGRAMME

TIME	MONDAY (10 DEC 2012)	TUESDAY (11 DEC 2012)	TIME	WEDNESDAY (12 DEC 2012)	TIME	THURSDAY (13 DEC 2012)
0800-0815		Conference Registration	0800-0815		0800-0815	
0815-0830			0815-0830		0815-0830	
0830-0845			0830-0845		0830-0845	Parallel Technical Paper Session 5 (I-III) Tea Break
0845-0900			0845-0900		0845-0900	
0900-0915		Opening Ceremony	0900-0915	Parallel Technical Paper Session 2 (I-III) Tea Break	0900-0915	
0915-0930			0915-0930		0915-0930	
0930-0945		Keynote Address **(Emeritus Professor Dr. Muhamad Awang)**	0930-0945		0930-0945	
0945-1000			0945-1000		0945-1000	
1000-1015			1000-1015		1000-1010	
1015-1030			1015-1030		1010-1030	Tea Break
1030-1045		Tea break	1030-1040		1030-1045	Parallel Technical Paper Session 6 (I-III)
1045-1100			1040-1100	Tea Break	1045-1100	
1100-1115		Plenary Lecture 1 **(Prof. Dr. Ji-Won Yang)**	1100-1115	Plenary Lecture 3 **(Prof. Datin Dr. Azizan binti Baharuddin)**	1100-1115	
1115-1130			1115-1130		1115-1130	
1130-1145			1130-1145		1130-1145	
1145-1200		Plenary Lecture 2 **(Prof. Dr. Kazunori Sato)**	1145-1200	Plenary Lecture 4 **(Assoc. Prof. Dr. J. Paul Chen)**	1145-1200	
1200-1215			1200-1215		1200-1220	
1215-1230			1215-1230		1220-1230	Best Poster Award and Closing Ceremony
1230-1245		Lunch Break	1230-1245	Lunch Break	1230-1245	
1245-1300			1245-1300		1245-1300	
1300-1315			1300-1315		1300-1315	Lunch
1315-1330			1315-1330		1315-1330	
1330-1345			1330-1345		1330-1345	
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1400-1415		Parallel Technical Paper Session 1 (I-III) Poster Presentation	1400-1415	Parallel Technical Paper Session 3 (I-III) Tea Break	1400-1415	
1415-1430			1415-1430		1415-1430	
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1445-1500			1445-1500		1445-1500	
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1515-1530			1515-1530		1515-1530	
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1545-1600			1540-1600	Tea Break	1540-1600	
1600-1615	Conference Registration	Poster Presentation	1600-1615	Parallel Technical Paper Session 4 (I-III)	1600-1615	
1615-1630			1615-1630		1615-1630	
1630-1645			1630-1645		1630-1645	
1645-1700			1645-1700		1645-1700	
1700-1715		Hi Tea	1700-1715		1700-1715	
1715-1730			1715-1740		1715-1740	

KEYNOTE SPEAKER

Green Technology and Sustainability in Agroindustry: Do we have enough R&D?

Emeritus Professor Muhamad Awang, FASC, JSM, Ph.D.

SEGi University
Kota Damansara, Petaling Jaya, Selangor.

Abstract

This presentation highlights some research and development initiatives carried out in Malaysia and other countries in the region in response to the issues with special emphasis on the sustainability of agroindustry and its energy utilisation in relation to greenhouse gas (GHG) emissions and climate change. One of the most important challenges identified during the course of the studies was the verification of gaps in the current scientific understanding of GHG emissions from agriculture with special reference to oil palm plantation that must be addressed to provide the agricultural industries with an adequate body of evidence about the relationships between practices and climate change, especially due to green house gas emissions. Some of the key features related to climate change scenario based on the latest assessment conducted by the working group of IPCC in relation to our GHG emission are also discussed.

PLENARY SPEAKERS

Plenary Lecture 1

The Current Activities of Advanced Biomass R&D Center in Korea

Professor Dr. Ji-Won Yang

Advanced Biomass R&D Center, 291 Daehakno, Yuseong-gu, Daejeon 305-701, Republic of Korea.
Professor, Department of Chemical and Biomolecular Engineering, KAIST, 291 Daehakno, Yuseong-gu, Daejeon 305-701, Republic of Korea.

Abstract

The ABC (Advanced Biomass R&D Center) was created by the funding from the Ministry of Education, Science and Technology (MEST), Republic of Korea and led by professor Ji-Won Yang in the Department of Chemical and Biomolecular Engineering at KAIST ($10 million/yr, 9 years). The ABC was created to identify key challenges and propose solutions to produce advanced biofuels and bioproducts that are economical and sustainable. The overall goal of the ABC is to develop, test, and transfer new technologies to commercial partners and others developing the advanced biofuels and white biotech industry. In order to achieve this goal, the ABC focuses on three major objectives: 1) the development of lignocellulosic and microalgal biomass feedstock, 2) the development of S&T for biomass production and downstream applications for biofuels and bioproducts, and 3) the systematic development and applications of biomass conversion technology for biofuels and bioproducts. The target biofuels and bioproducts include ethanol, buthanol, isobuthanol, biodiesel, and hydrocarbons, and aromatic compounds, muconic acids, and 3-HP, respectively. As the original organizer and lead institute of ABC, KAIST has been developing technologies for algal cultivation, harvest, extraction, conversion, algal genetic transformation, and systems metabolic engineering of microalgae. A research team at KASIT also has been developing technologies for algal cultivation in wastewater. In this presentation the membership, technical highlights of ABC and the current algal biofuels and bioproducts researches in my laboratory will be discussed. (**This work was supported by grants from the Advanced Biomass R&D Center in the Global Frontier Program from the Korean Ministry of Education, Science & Technology**)

Plenary Lecture 2

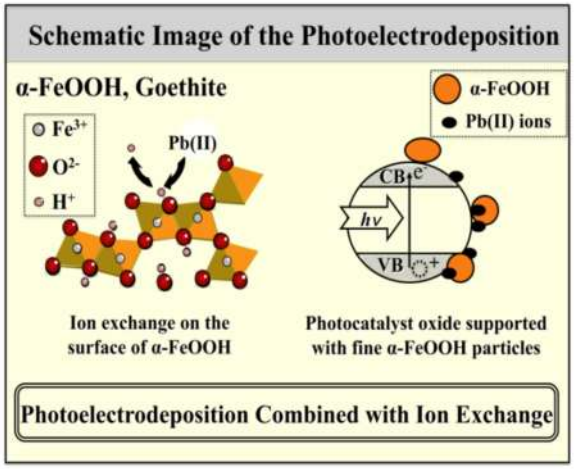
The role of photocatalyst materials for the recovery of heavy metal ions in an aqueous environment

Professor Dr. Kazunori SATO

Director, Center for International Exchange and Education
Professor, Department of Environmental Engineering (Materials Science)
Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan.

Abstract

In order to remove hazardous heavy metal ions dissolved in an aqueous environment, the photoelectrodeposition effect combined with an inorganic ion exchanger, α-FeOOH, on the removal of Pb(II), Cu(II), and Zn(II) ions has been investigated for photocatalyst materials based on titania and ceria. These materials showed the highest photoelectrodeposition ability for Pb(II) ions under the photo irradiation, whose schematic image is shown in the figure below. The removal efficiency of Pb(II) ions was high under the UV irradiation and it decrased with increasing the wavelength of light toward the visible region. This result indicates that the coexistence of fine α-FeOOH particles with the oxide particles contributes to an efficient separation of holes and electrons generated by the photo irradiation. The high-resolution scanning electron microscopic observation revaled that fine α-FeOOH particles supported on the surface of the oxide particles are effective for the charge separation between holes and electrons. This effect is probably caused by the redox reaction occurring for the transfer of electrons near the interface between α-FeOOH and the oxide particles. A possible mechanism for the efficient removal of hazardous heavy metal ions dissolved in an aqueous environment is presented.



Plenary Lecture 3

Giving Values to Science, Technology and Engineering for Sustainability

Professor Datin Dr. Azizan binti Baharuddin

Deputy Director - General
Institut Kefahaman Islam Malaysia (IKIM)
2, Langgak Tunku, Off Jalan Duta, 50480 Kuala Lumpur, Malaysia.

Abstract

Currently there is a gap between ideas that promote the infusing of values into science, technology and engineering and those that see knowledge and applications of science, technology and engineering as producers and promoters of values to begin with. Are the 'values' spoken of by these two groups the same in their intent and effect or do they bespeak of contending worldviews that needs bridging and harmonizing to begin with? Is it possible for "sacred" principles to be appreciated by those refusing interference from "non-empirical" epistemologies? Current research and analyses of the relationship between science and culture/religion seems to indicate that it is possible to have reenchantment (respect, awe, care and love of the environment) without grievous supernaturalism (extreme rejection of reason).

Plenary Lecture 4

Adsorption and membrane filtration for water treatment

Associate Professor Dr. J. Paul Chen

Associate Professor,
Department of Civil and Environmental Engineering
National University of Singapore

Abstract

Due to industrialization, both surface and ground water has severely been contaminated. However, the demand for safer water has been increased in the last ten years. Water has become one of most important resources in the world. In this talk, a series of novel materials and technologies of adsorption and membrane filtration will be presented. The working mechanisms will be discussed in details. Important developments such as highly cost-effective adsorbents and affinities membrane will be addressed for the removal of toxic contaminants (e.g., arsenic and copper). Mathematical models such as surface complex formation model and ion exchange model for better understanding of adsorption processes will be introduced. Several industrial cases will be presented.

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SECTION 3: NOVEL SOLUTIONS AND SUSTAINABLE TECHNOLOGIES FOR THE BENEFITS OF BOTTOM BILLIONS

SECTION 4: AIR POLLUTION MITIGATION, MONITOR, CONTROL TECHNOLOGIES

SECTION 5: LIFE CYCLE ASSESSMENT, RISK ASSESSMENT, HEALTH AND SAFETY IMPACT ASSESSMENT

SECTION 6: ADVANCES IN NATURAL RESOURCE EXPLOITATION AND UTILIZATION

SECTION 7: INNOVATIVE TECHNOLOGIES AND NEW DIRECTIONS IN SOLUTION OF ENVIRONMENTAL ISSUES

SECTION 8: ISSUES OF ENERGY IN SUSTAINABLE DEVELOPMENT

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International Conference on Environment 2012 (ICENV 2012)
11-13 December 2012
Penang, Malaysia

KINETIC AND THERMODYNAMIC INFLUENCE ON ADSORPTION OF BASIC DYE FOR ENVIRONMENTAL SUSTAINABILITY

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ABSTRACT

The rate and mechanism of pollutants removal as a means of serene environment sustainability was investigated. This was done through adsorption of Basic Blue 3 dye pollutant using environmentally friendly raw and chemically activated waste tea adsorbent. The study involved equilibrium, isotherm, kinetic and thermodynamic study of the adsorption process. The adsorption processes were best described by pseudo-second-order kinetic model; the processes were spontaneous and exothermic in nature. Intra-particle diffusion mechanism was the rate limiting step. The modified waste tea gave higher adsorption capacity (176.16 mg/g) and was faster in BB3 removal from aqueous solution than the raw waste tea adsorbent (84.74 mg/g). Waste tea adsorbent can be used to contribute immensely towards environment sustainability.

Key word: Diffusion, Adsorption, Activation, Waste tea, Dye

1.0 Introduction

The impact of green technology globally which emanated some few decades ago is immense and its consciousness should be cherished like heart beats in every sane individual if the world dream of sustainable tomorrow is to be achieved. This material based technology has tried to reduce global warming and curb depletion of natural resources as well cater for the well being of all living things but there has been series of challenges in implementation in Malaysia and other parts of the world (Chua and Oh, 2011, Schreurs, 2012). But man's intrusion through technological advancement has outweighed mitigating measures put in place through green technology. Pollutants such gases, heavy metals, dyes, spills of oil and so on introduced to the environment due to anthropogenic activities not only serve as menace but also negatively affects plants, humans, animals whether in aquatic or terrestrial region (Ahmad and Alrozi, 2010).

Colors are used for identification, as styles, to determine economic position and even connote ones class. These and many reasons have geared man's love for colors and have gone beyond harnessing the natural existing dyes into synthetically producing it. Approximately 10,000 varieties of dyes and pigments are available and 70,000 tons of the dyes are produced annually (Auta and Hameed, 2011). Indiscriminate discharge of dyes (10-15 %) as pollutants alters the

physico-chemical parameters from the existing levels of the receiving body; this in turn has an adverse effect (Iqbal and Ashiq, 2007). Most synthetic dyes are known for their resistance to biodegradation, some adverse effects of plants photosynthesis in aquatic region and carcinogenic and mutagenic effects on humans (Cicek N. et al., 2012). Dyes are generally classified into anionic (acidic, direct and reactive), non-anionic (disperse) and cationic (azo basic, anthraquinone disperse) dyes (Turabik, 2008).

In pursuance of green technology objectives, many methods have been devised to salvage the ecosystem from dye pollution, this include biological treatment, coagulation, flotation, adsorption, oxidation and hyper-filtration. Quite an effect has been felt by each of this method but not without some challenges that negates their efficiency. Several researches have been carried out with a view to producing cheaper and renewable alternative adsorbents that will replace the pricey commercial activated carbon which adversely increases the cost of applying adsorption process for pollutants remediation (Nasuha et al., 2010).

This research is aimed at looking inwardly to harness possible cheaper adsorbents that can help in salvaging menace of basic dye (Basic Blue 3) pollution as part of contribution to green technology for sustainable tomorrow. The study will involve evaluating the equilibrium, isotherm, kinetic and thermodynamic mechanisms of the process.

2.0 Materials and method

Basic Blue 3 dye (BB3) was purchased from Sigma-Aldrich (M) Sdn Bhd, Malaysia, hydrochloric acid (HCl) and sodium hydroxide (NaOH) were obtained from Merck chemical company, Malaysia; all the chemicals were of analytical grade and used without any purification. Waste tea was taken from Cafeteria of Engineering campus, Universiti Sains Malaysia. The chemical structure of BB3 (molecular weight 359.89 g/mol) is shown in Fig. 1.

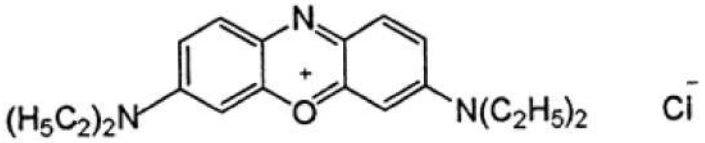

Fig. 1 Chemical structure of Basic Blue 3 dye

2.1. Adsorbent preparation method

The raw waste tea was washed thoroughly with boiled water until the supernatant became colorless and dried in an oven set at 110 ^{o}C for 24 h, sieved into 300-500 μm particle sizes and then packaged. Some quantity of the raw dried waste tea (RWT) was treated with 5 M HCl and allowed for 72 h to dwell. Thereafter, it was dried in an oven for 24 h, packaged and labeled as MWT (modified waste tea).

2.2. Equilibrium adsorption studies

To a set of Erlenmeyer 250 mL flasks containing 100 mL of different concentrations (40-200 mg/L) of BB3 was added 0.5 g of the adsorbent (RWT and MWT). The flasks were placed in isothermal water bath shaker set at 30 ^{o}C, 140 rpm for 10 h to allow for attainment of equilibrium. Before equilibrium stage, the residual dye concentration in the solution was determined at intervals with the of a double beam UV – vis spectrophotometer (Shimadzu, Model UV 1601, Japan) at maximum wavelength λ_{max}, 654 nm; this was to determine the kinetic of the sorption process. The amount of BB3 adsorbed at intervals of time, q_t (mg/g) was determined by:

$$q_t = \frac{(C_o - C_t)V}{W} \quad (1)$$

While amount of BB3 adsorbed at equilibrium q_e (mg/g) was calculated by:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (2)$$

where C_o and C_e (mg/L) are the initial and equilibrium concentration of BB3, V (L) is volume of the solution and W (g) is mass of the adsorbent.

2.3. Effect of pH of the solution

In a similar set up as the equilibrium experiment at 120 mg/L, the solution initial pH 2-12 was varied to study its effect on the adsorption process. 0.1 M of both NaOH and HCl were used to initialize the solution pH which was ascertained by using pH meter (Ecoscan, EUTECH Instruments, Singapore).

3.0 Results and discussion

3.1. Effect of pH on BB3 adsorption

Adsorption of BB3 both RWT and MWT was much better at higher pH as can be seen in Fig. 2. Low adsorption at lower pH 2-4 could be due to repulsive activities between the amino groups of BB3 with the protons of the solution, while electrostatic attraction activities may have dominated the higher pH where adsorption was enhance, similar observation has been reported (Nasuha et al., 2010, Hameed, 2009).

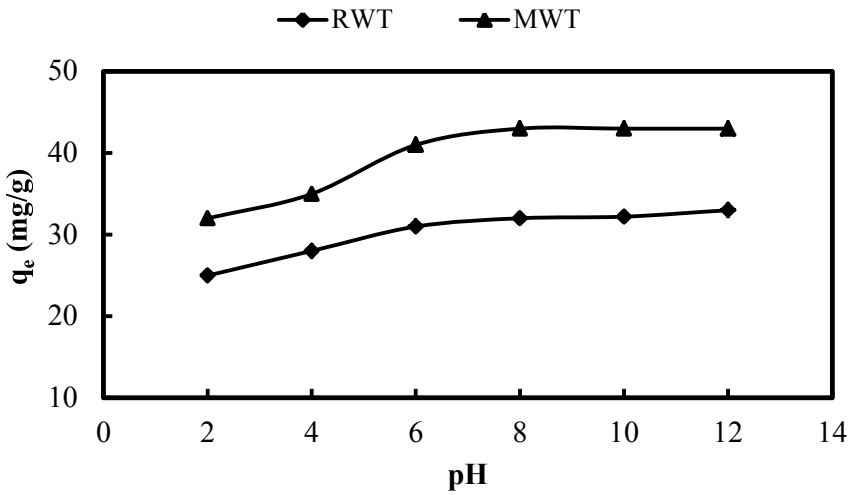

Fig. 2 Effect of solution pH on adsorption of BB3 by RWT and MWT at 30 ^{o}C

3.2. Effect of initial concentration on BB3 adsorption

Increase in driving force that is concentration gradient lead to higher adsorption of BB3 on the adsorbent, high solute concentration occupied the readily available numerous vacant site on the adsorbent. Adsorption of BB3 increased in amount from 14.38 to 50.28 mg/g on RWT and 16.22 to 62.32 mg/g on MWT. Higher percentage of adsorption was observed when lower initial concentration of solution was used, this may be attributed to limited or inadequate solute molecules in the solution which were outstripped by the vacant sites on the adsorbent. A differential of 18 and 25% for RWT and MWT adsorbents, respectively were observed as the percentage increase of adsorption when initial concentration of the solution were varied between 40 and 200 mg/L. Proportionality of increase in adsorption with corresponding concentration increase and higher percentage adsorption with lower initial solute concentration has been reported (Auta and Hameed, 2011).

3.3. Adsorption equilibrium isotherm studies

Langmuir (Langmuir, 1916), Freundlich (Freundlich, 1906) and Temkin (Temkin and Pyzhev, 1940) equilibrium isotherm models were used to investigate the interaction pattern between the sorbent and sorbate. The non-linear equations of Langmuir (3), Freundlich (4) and Temkin (5) are expressed as follows:

$$q_e = \frac{q_m C_e b}{(1+bC_e)} \quad (3)$$

$$q_e = k_f C_e^{1/n} \quad (4)$$

$$q_e = B\ln(k_T C_e) \quad (5)$$

where C_e (mg/L), is the equilibrium concentration of BB3 adsorbed; q_e (mg/g), is the amount of MB adsorbed; q_m (mg/g) and b (L/g) are the Langmuir constants representing monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively; the Freundlich constants are K_F

((mg/g) $(L/mg)^{1/n}$) and 1/n (values of n>1 represents favorable adsorption condition) which connotes amount adsorbed and adsorption intensity, respectively; Temkin constant k_T (L/mg), is for equilibrium binding constant correlating the maximum binding energy while $B=RT/b_T$; where R is Universal gas constant (8.314 J/mol K), T (K) is absolute temperature and b_T (J/mol) is related to heat of adsorption.

Analysis of the isotherm models showed that Langmuir model best described BB3 adsorption on both RWT and MWT and the least was by Temkin model as shown in Table 1. The inconsistency of the correlation coefficient R^2 for justification of the best model necessitated use of Chi square (χ^2) statistical method to adjudged the best fitting model, inability of R^2 to determine best fit model has been reported (Azizian and Yahyaei, 2006). The best fitted model was selected based on the least χ^2 values of which Langmuir model had the least values in magnitude while Temkin parameters model χ^2 values were larger. Similar adsorption trend was observed when methylene blue was adsorbed on spent tea leaves (Hameed, 2009). Conformation of Langmuir equilibrium isotherm model to BB3 adsorption on both adsorbents denotes the followings: the BB3 adsorption took place on specific homogeneous sites within the adsorbent, and upon adsorption of a molecule on any active site no further adsorption was allowed by the site, all active sites were energetically equivalent and identical, and no interaction between adsorbed molecules took place. The Freundlich isotherm model's parameters revealed that the dimensionless constant 'n' had values greater than unity (n>1) signifying favorability of physical adsorption process of BB3 on the adsorbents (Treybal, 1987). The assertion by Temkin model that because of some indirect adsorbate/adsorbate interactions on adsorption isotherms that heat of adsorption of all the molecules in the layer would linearly decrease with coverage did not hold on BB3 adsorption process. This was because the adsorbed molecules on the surface of the adsorbent did not interact and as such the heat of adsorption of BB3 molecules had no effect on each other couple with the fact that the energy on layers was universally and evenly distributed.

Chi square statistical analysis was carried out using equation (6):

$$\chi^2 = \frac{\sum(q_{e,meas}-q_{e,cal})^2}{q_{e,meas}} \qquad (6)$$

where $q_{e,meas}$ is the experimental q_e calculated and $q_{e,cal}$ is the predicted model q_e data obtained.

Table 1 Langmuir, Freundlich and Temkin isotherm models parameters at 30 ^{o}C

Model	Kinetic parameters	RWT	MWT
Langmuir	q_e (mg/g)	84.74	176.16
	k_L(L/mg)	0.0157	0.0343
	R^2	0.995	0.987
	χ^2	3.72	2.15
Freundlich	k_F((mg/g)(L/g))1/n	3.800	5.828
	1/n	0.565	0.553
	R^2	0.968	0.999
	χ^2	3.88	2.34
Temkin	A (L/g)	0.190	0.266
	B	16.354	20.054
	R^2	0.977	0.988
	χ^2	4.819	5.117

3.3. Kinetics of BB3 adsorption on RWT and MWT

Two kinetic models pseudo-first-order (Lagergren, 1898) and pseudo-second-order (Ho, 1999) were tested to determine the best fitted model to the BB3 adsorption on RWT and MWT data. The non-linear form of pseudo-first-order (7) and pseudo-second-order (8) models equations are given as:

$$q_t = q_e(1 - e^{-K_1 t}) \quad (7)$$

$$q_t = \frac{K_2 q_e^2 t}{(1+K_2 q_e t)} \quad (8)$$

where q_e and q_t (mg/g), are the amount of BB3 adsorbed at equilibrium and at time t (h), respectively; k_1 (h^{-1}) and k_2 (g/mgh) are the rate constants pseudo-first-order and pseudo-second-order kinetic models, respectively. The models parameters generated from their plots (figures not shown) are summarized in Table 2.

The two kinetic models analysis for BB3 adsorption on the two adsorbents showed pseudo-second-order model best described the adsorption process. This was due to closer to unity nature of their R^2 values even though the differences were insignificant. The Chi square analysis further justified the fitness of the model as its Chi square values were smaller as can be seen in Table 2. Pseudo-second-order model described the entirety of adsorption process as against pseudo-first-order which is limited to initial stage of adsorption process. Faster rate and higher adsorption capacity of BB3 on MWT (180 min) than on RWT (300 min) were observed, it could be attributed to modification or treatment of the waste tea with hydrochloric acid. It has been reported that treatment of carbonaceous material with HCl not only help in evacuating some inorganic contents, but helps in improving the surface area as well as increasing accessibility to the carbonaceous content of the material (Ros et al., 2006, Ros A. et al., 2007).

Table 2 Adsorption kinetic models parameters at 30 °C

Model	Parameters	Initial BB3 concentration (mg/L)				
		40	80	120	160	200
RWT	q_{exp} (mg/g)	14.38	25.26	35.71	42.20	50.28
Pseudo-first-order	k_1(min^{-1})	0.0115	0.0122	0.0143	0.0183	0.0164
	$q_{e\,cal}$ (mg/g)	29.51	52.59	73.41	86.43	111.35
	R^2	0.9918	0.9965	0.9908	0.9905	0.9953
	χ^2	0.68	1.18	6.17	8.64	7.13
Pseudo-second-order	k_2 (g mg^{-1} min^{-1}) x10^4	4.36	1.84	1.72	1.99	1.39
	$q_{e\,cal}$ (mg/g)	36.00	65.96	89.20	102.62	132.95
	R^2	0.9942	0.9967	0.9910	0.9913	0.9955
	χ^2	0.37	1.26	6.06	1.45	5.39
MWT						
Pseudo-first-order	q_{exp} (mg/g)	16.22	30.18	43.09	53.33	62.34
	k_1(min^{-1})	0.0207	0.0162	0.0175	0.0273	0.0218
	$q_{e\,cal}$ (mg/g)	34.18	61.70	86.50	102.67	127.68
	R^2	0.9793	0.9691	0.9504	0.9823	0.9703
	χ^2	2.89	13.99	42.40	21.71	56.18
Pseudo-second-order	k_2 (g mg^{-1} min^{-1}) x10^4	6.51	2.63	2.19	3.13	1.94
	$q_{e\,cal}$ (mg/g)	39.47	72.93	100.30	115.73	145.90
	R^2	0.9939	0.9911	0.9744	0.9977	0.9902
	χ^2	0.85	4.01	21.84	2.86	18.50

3.4. Adsorption mechanism

Weber and Morris (Weber and Morris, 1963) equation was used to determine the actual mechanism of sorption of BB3 on the adsorbent as the kinetic models only relay order of the process. The equation often termed intra-particle diffusion model expresses diffusion of components dependency on time. It postulates that if sorption process is dependent on adsorbate-adsorbent interaction, then the process is diffusion controlled (Toor and Jin, 2012). The intra-particle diffusion model is expressed as:

$$q_t = k_{Pi} t^{0.5} + C \quad (9)$$

where, kpi (mg/(g $min^{0.5}$)) is the intra-particle diffusion rate constant, and C relays information about the boundary effect. The models parameters generated are summarized on Table 3. The plots q_t against $t^{0.5}$ gave two features (figures not shown) for both RWT and MWT adsorption of BB3. The steeper section represents the boundary layer diffusion with kp1 as the intra-particle diffusion parameter while the slower and gradual flattened segment represents the intra-particle diffusion region with k_{p2} as its diffusion parameter. The k_{p2} (intra-particle diffusion parameter) values for the two adsorbents were smaller than those of k_{p1} (boundary layer diffusion); this reflects lesser collision of BB3 molecules at this stage thereby limiting the rate of adsorption. More so, intra-particle boundary effect C was more immense than that of boundary layer diffusion effect; this is seen by the larger values of C (Li et al., 2010a).

Table 3 Parameters generated from intra-particle diffusion model

Initial Conc. (mg/L)	Boundary k_{p1}(mg/g $min^{½}$)	Layer C_1	Diffusion R^2	Intra-particle k_{p2} (mg/g $min^{½}$)	diffusion C_2	R^2
RWT						
40	1.27	9.84	0.985	0.32	23.74	0.986
80	3.28	12.57	0.995	0.47	42.76	0.999
120	3.80	17.31	0.977	0.50	64.31	0.974
160	3.09	40.98	0.943	0.88	71.02	0.901
200	4.94	38.34	0.939	0.94	105.20	0.982
MWT						
40	2.65	1.95	0.981	0.54	25.54	0.916
80	4.26	3.39	0.986	1.10	35.17	0.986
120	5.63	9.35	0.992	1.16	67.54	0.913
160	8.02	12.19	0.976	1.06	87.02	0.959
200	9.49	19.02	0.995	1.62	102.50	0.983

3.5. Thermodynamics studies of the adsorption process

Gibbs free energy ΔG, enthalpy ΔH and entropy ΔS thermodynamic parameters were studied to determine the nature of the adsorption process. Van't Hoffs equation was used to determine the Gibbs free energy, it is expressed as:

$$\Delta G = -RTIn\ K_o \quad (10)$$

where R is the universal gas constant (8.314 J/Kmol); T (K) the absolute temperature; K_o is the distribution coefficient expressed as $K_o=q_e/C_e$.

Standard enthalpy change of BB3 adsorption on RWT and MWT were determined with rearranged Van't Hoff equation given as:

$$InK_o = \frac{-\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (11)$$

The values of ΔH and ΔS were obtained from the plot of InKo against 1/T (figures not shown) as shown in Table 4.

Table 4 Thermodynamic parameters for RWT and MWT adsorption of BB3

Adsorbent	ΔH (J/mol)	ΔS (J/mol)	ΔG (J/mol)		
			303 K	313 K	323 K
RWT	-1154	29.41	-2167	-1962	-1750
MWT	-13319	40.47	-3898	-3257	-3012

Sorption of BB3 on RWT and MWT were all spontaneous but with less severity on the surface of RWT. The sorption process increased with decrease in temperature signifying exothermic and physical nature of the adsorption; this is due to magnitude of enthalpy values which were less than 20 kJ/mol (Li et al., 2010b). Similar observation has been reported for dye adsorption on adsorbent surface (Auta and Hameed, 2011).

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Conclusion

Two adsorbents, raw and modified (HCl) waste tea were prepared and tested for BB3 removal from aqueous solution through batch adsorption process. The adsorption of BB3 by the adsorbents was best described by Langmuir isotherm model, pseudo-second-order model, and was also found to be exothermic and spontaneous. The MWT adsorbent had higher adsorption capacity (176.16 mg/g) than RWT (84.74 mg/g), faster rate of adsorption and more spontaneous. Intra-particle diffusion mechanism was the limiting step for BB3 adsorption on both surfaces of the adsorbents. This research has revealed that waste tea adsorbent can be employed in BB3 pollutant remediation as part of green technology measure towards sustainable tomorrow.

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