IJARSCT

ISSN (Online) 2581-9429

International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

Impact Factor: 7.301

Volume 3, Issue 1, April 2023

Adsorptive Studies of Toxic Lead Ions and Methylene Blue from Aqueous Solution by Black Eyed Beans

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Abstract: *In this study Black eyed beans were used for the removal of toxic Pb(II) ions and methylene blue dye from aqueous solution. The use of Black eyed beans in water treatment application is largely unexplored. Therefore the current study is the first ever to report on Black eyed beans as potential adsorbents. Black eyed beans were tested as adsorbents in pristine and chemically treated form. Batch adsorption experiments were conducted to evaluate the effect of systematic parameters such as the initial concentration, temperature, contact time and pH. The adsorbents were characterized by scanning electron microscope (SEM), thermogravimetric analysis (TGA), X-ray diffraction (XRD), fourier transformed infrared (FTIR) and Brunauer-Emmet teller (BET). SEM images revealed that acetone treated Black eyed beans (Ac-MB), methanol treated Black eyed beans(Me-MB) and dimethyl formamide treated Black eyed beans(DMF-MB) morphologies were dominated by spherical microstructures. FTIR analysis affirmed the presence of oxygen containing functional groups such as (–OH), (–COOH) and (–C]O) attached to the adsorbents surface. These groups could enhance the adsorption processes. BET results also suggested that treated Black eyed beans exhibits large pores, which could easily trap Pb(II) ions and methylene blue dye. It was observed that uptake of Pb(II) and methylene blue increased with increase in initial concentration of solution. However, all adsorbents had higher adsorption capacity for methylene blue molecules than Pb(II) ions. Also adsorption rate of methylene blue was faster, achieving equilibrium in 20 min and Pb(II) ions in 90 min. Enhancing the temperature of the solution had a positive effect on the removal of Pb(II) ions by UT-MB and AcMB, while for methylene blue it was Me-MB and Ac-MB revealing the exothermic nature of the processes. However, increasing the temperature was detrimental on the adsorption of Pb(II) ions onto Me-MB, AA-MB and DMF-MB, for methylene blue it was onto DMF-MB, UT-MB and AA-MB revealing the endothermic nature of the processes. The maximum adsorption capacities were obtained at pH 9 for both pollutants, Pb(II) adsorption capacity trends were UT-MB > Ac-MB > DMF-MB > AA-MB > Me-MB (19.96, 18.94, 17.60, 16.17 and 16.15 mg/g) respectively and for methylene blue were Me-MB > DMF-MB > UT-MB > Ac-MB > AA-MB (24.56, 23.89, 22.86, 22.78 and 22.55 mg/g). Pb(II) adsorption onto all adsorbents fitted Freundlich model. Methylene blue adsorption onto UT-MB and Ac-MB fitted Langmuir model, while Me-MB, AA-MB and DMF-MB fitted Freundlich model. Kinetic studies revealed that all adsorption processes found good fit for PSO model. However, Pb(II) ions adsorption onto AA-MB and DMF-MB had good fit for PFO model.*

Keywords: Black eyed beans

I. INTRODUCTION

In the last century many products such as medicines, disinfectants, laundry detergents, paints, surfactants, pesticides, dyes, preservatives, personal care products, and food additives have been found to be threatening to human as well as the environment [1, 2]. Various industries like fuel production units, atomic energy stations, electroplating and fertilizer industry, leather and electrical appliance manufactory, and iron enterprises generate enormous wastes containing large amount of toxic heavy metals discarded into the environment resulting in ecological imbalance. The pollutants and decaying organic matter in waste water take up the dissolved oxygen and excessive nutrients like phosphorus and nitrogen cause eutrophication which promotes excessive plant growth and reduces available oxygen in the water body. Bacteria, viruses and disease-causing pathogens also pollute beaches and contaminate shellfish populations, leading to restrictions on human recreation and drinking water consumption. Metabolism dependent and independent processes can also result in the accumulation of large amount of metals [3] and trigger the free radical response leading to oxidative stress [4].

II. EXPERIMENTAL SECTION

2.1. Materials and Methods

Black eyed beans were purchased from a local health shop. Methanol (CH3OH)–99.8% A.R grade, N,N–Dimethylformamide (HCON(CH3)2)–99.8% A.R grade, acetic acid (CH3COOH)– 99.85% A.R grade and acetone (C2H6CO)–99.5% .

2.2 Preparation Of Bio-Adsorbents

2.2.1. Untreated Black Eyed Beans (UT-BCS) Adsorbent Preparation

Dried black eyed beans were purchased from a local health shop. 500 g beans were soaked in distilled water, oven dried for 2h and then ground. The grounded beans were soaked in water then further dried in an oven for 72h and labeled untreated black eyed beans (UT-BEB).

2.2.2. Acetic Acid Treated Black Eyed Beans (AA-BEB) Adsorbent Preparation

UT-BEB (10 g) was treated with 100 ml of concentrated acetic acid for 60 min. After time elapsed the material was soaked in distilled water to wash excess acid then oven dried and labelled; acetic acid treated black eyed beans (AA-BEB)

2.2.3. Acetone Treated Black Eyed Bean (AC-BEB) Adsorbent Preparation

UT-BEB (10 g) was mixed with acetone (100 ml) for 60 min to extract some of the acetone soluble compounds attached to the surface of black eyed beans. After 60 min the material was filtered, oven dried and then labelled; acetone treated black eyed beans (Ac-BEB).

2.2.4. Dimethylformamide (DMF) Treated Black Eyed Bean (AC-BEB) Adsorbent Preparation

10 g of UT-BEB was mixed with 100 ml of DMF for 60 min. The obtained slurry material was centrifuged, oven dried for 12 h and then labelled; dimethylformamide treated black eyed beans (DMF-BEB).

2.2.5. Methanol Treated Black Eyed Bean (ME-BEB) Adsorbent Preparation

10 g UT-BEB was mixed with methanol (100 ml) for 60 min. After 60 min the material was filtered, oven dried and then labelled; methanol treated black eyed beans (Me-BEB).

2.3. Adsorption Experiments

Lead nitrate ($Pb(NO_3)$) and methylene blue stock solutions (100 mg/ L) were prepared by dissolving 0.1 g of respective salts in 1 L of distilled water. Effect of time; was studied at time intervals (1, 5, 10, 30, 60 and 120 min) with standard solution of concentration (100 mg/L). The

standard solution (20 ml) was transferred into bottles containing 0.1 g of the adsorbent. Effect of the initial concentration; was studied on standard solutions of (20, 40, 60, 80 and 100 mg/L) at time interval 120 min. 20 ml of the standard solutions were transferred into bottles containing 0.1 g of the adsorbent. Effect of temperature; was studied at 25 °C (298 K), 30 °C (303 K), 40 °C (313 K), 60 °C (333 K) and 80 °C (353 K) using the standard solution of 100 mg/L 20 ml of the standard solution was transferred into bottles containing 0.1 g of the adsorbent at specified temperatures. pH effect was evaluated at varying pH (1, 3, 5, 7 and 8.5) of the solution. 20 ml of the working standard (100 mg/L) was transferred into capped bottles containing 0.1 g of the adsorbent. An orbital shaker was used for all experiments to equilibrate the working standard and adsorbent at 200 rmp. After each experiment, respective capped bottles were removed, and then centrifuged for 5 min at 4500 rpm. The solution was taken for analysis of Pb(II) and methylene blue remaining. The concentrations of Pb(II) and methylene blue working standards before adsorption and supernatant solutions after adsorption were confirmed by ICP and UV respectively. All adsorption studied were conducted in batch experimental mode.

2.4. Regeneration Procedure

Regeneration of black eyed beans adsorbents was conducted by treating the previously used adsorbent in 20 ml 0.3 M HNO3 at 200 rpm for 30 min and then rinsed several times with ultra-pure water at 200 rpm for 60 min before reuse.

III. CHARACTERIZATION

The adsorbents; surface morphology, thermal stability, functional groups, nitrogen adsorption/desorption and the phase purity were confirmed by SEM, TGA, FTIR, BET and XRD techniques respectively. Scanning electron microscopy (SEM) images were taken on a Nova Nano SEM 200 from FEI operated at 10.0 kV. Perkin Elmer Fourier transformed infrared spectroscopy FTIR/FTNIR spectrometer, spectrum 400 was used. X-ray diffractometer (XRD), Shimadzu XRD 7000 was used to identify crystalline phase of the sample, scan range was set from 10 to 80 (2θ °), scan speed was set at 10°/min. Thermo gravimetric analyzer (TGA), a Perkin Elmer TGA 4000 was used: analyses were performed from 30 to 900 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. Inductive couple plasma spectroscopy (ICP), thermo scientific iCAP 7000 series, ICP spectrometer, using ASX-520 auto sampler, was used to measure the metal ion solutions before and after adsorption. BET specific surface area of the adsorbents was evaluated by nitrogen adsorption/desorption. UV–Vis analyses were performed with a double beam spectrometer - Perkin Elmer Lambda 25 UV/Vis, which collects spectra from 180 to 1100 nm UV and visible range using a slit of 1.0 and width of 0.1. A lamp of tungsten and deuterium were used to provide illumination. A baseline setting was done by using water as a reference sample. The pH of the samples was determined in deionized water, and pH at point of zero charge pH(PZC) was evaluated using the pH drift method.

3.1. Physicochemical Characterization

3.1.1. pH, Point Zero Charge and Nitrogen Adsorption/Desorption Studies

It was observed that ph(PZC) values of Me-BEB, Ac-BEB, AA-BEB and DMF-BEB were lower than that of UT-BEB. The pH(PZC) values of all adsorbents were on the acidic region. All adsorbents acquired positive charge on the surfaces at pH values below their pH(PZC). However at pH values above their respective pH(PZC) surfaces were negatively charged. It was observed that UT-BEB had BET surface area of 3.52 m2/g with pore width of 3.79 nm. The BET surface area of DMF-BEB, Me-BEB and AA-BEB increased to 319, 277 and 269 m2/g respectively, Maurya et al. (2015), also observed increase in surface area when biomass are chemically treated. Me-BEB, AA-BEB and DMF-BEB pore width also increased to 4.27, 4.33 and 4.27 nm. Ac-BEB surface area and pore width slightly reduced.

TABLE 1: Data of Adsorbents

Physicochemical parameters of the adsorbents.

Adsorbent	$pH_{(H2O)}$	$pH_{(PZC)}$	BET surface area (m^2/g)	Pore size (cm^2/g)	Pore width (nm)
UT-BEB	7.08	5.43	3.52	0.00479	3.79
Me-BEB	6.93	5.31	277	0.312	4.27
Ac-BEB	6.72	5.15	0.167	0.00139	3.01
AA-BEB	4.56	3.49	269	0.306	4.33
DMF-BEB	6.49	4.97	319	0.361	4.27

3.2. Adsorbents Characterization

3.2.1. Sem Analysis

The surface characterization of untreated and treated BEB was carried by analyzing the SEM images presented in Fig. 4a–j. The UT-BEB and AA-BEB morphological feature presented in Fig. 4a–b and 1c-d respectively shows larger particles that are irregular in nature which is generally observed in beans (Ferreira et al., 2019). However, differences can be identified in SEM images of Ac-BEB, Me-BEB and DMF-BEB presented in Fig. 4e–f, 1g-h and 4i-j respectively, the surface morphology show irregular small particles with spherical microstructures dominating.

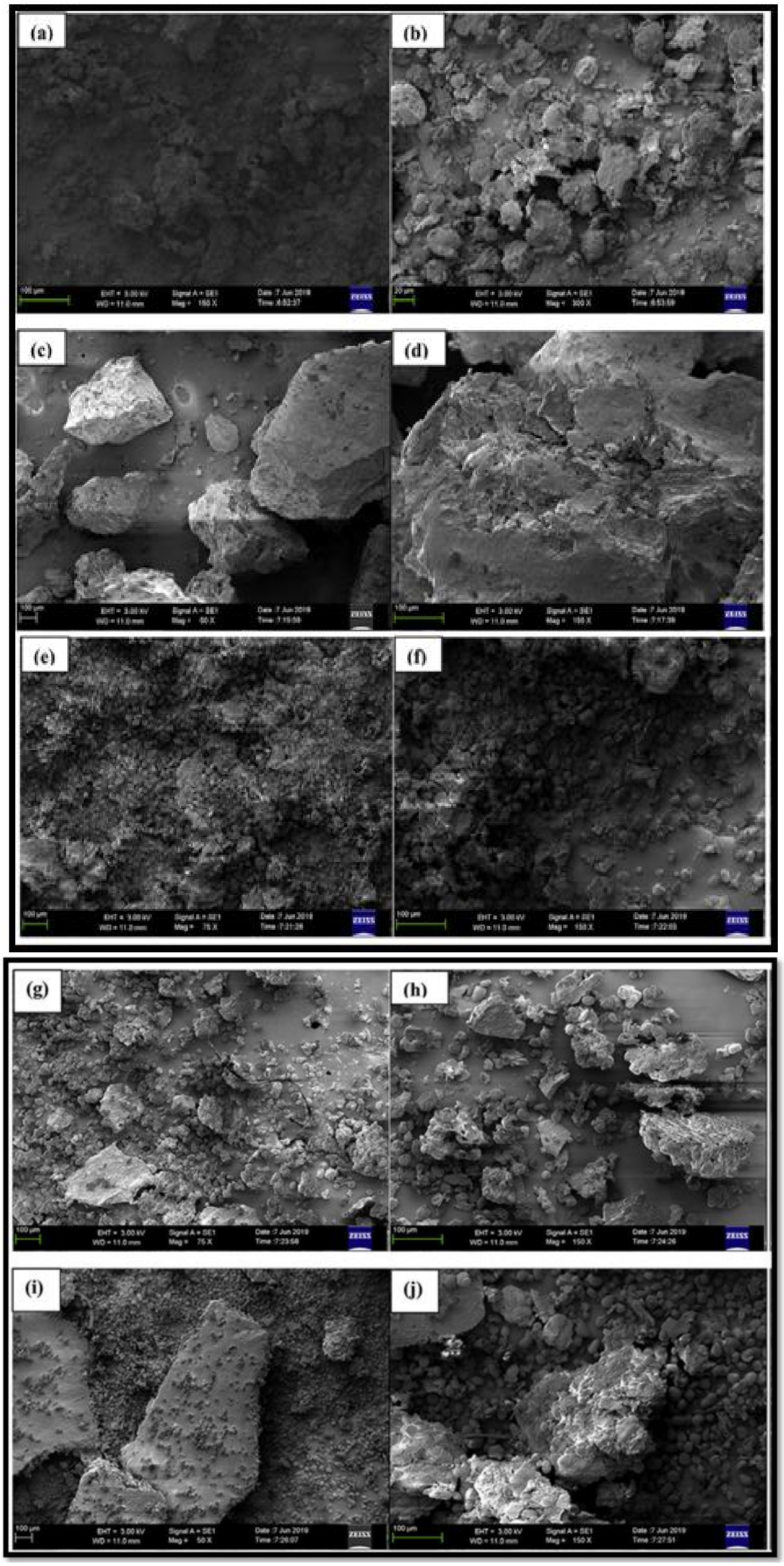

FIG 1. SEM IMAGES OF (A-B) UT-BEB, (C-D) AA-BEB, (E-F) AC-BEB, (G-H) ME-BEB AND (I-J) DMF-BEB.

IJARSCT

ISSN (Online) 2581-9429

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Impact Factor: 7.301

3.2.2 XRD Analysis

XRD plots of UT-BEB, Me-BEB, Ac- BEB, AA-BEB and DMF-BEB are depicted in Fig. 2. Crystalline lignocellulose materials in the adsorbents are assigned to broad peak indexed (002) and the amorphous nature of the adsorbents is assigned to weak peaks indexed (040).

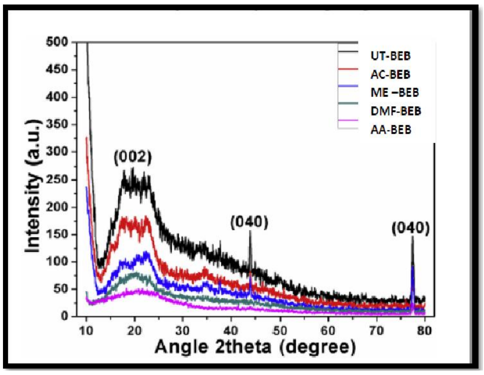

Figure 2 XRD Of Adsorbents.

3.3. Adsorption Studies

Table. 2 Comparison of langmiur and freundlich isotherms for Pb(II) and methylene blue adsorption onto black eyed beans adsorbents

Isotherms		UT-BEB		ME-BEB		AC –BEB		AA-BEB		DME-BEB	
		Pb(II)	Methyl B	Pb(II)	Methyl B	Pb(II)	Methyl B	Pb(II)	Methyl B	Pb(II)	Methyl B
Langmuir	Q_o	19.26	19.97	14.10	19.81	18.25	19.66	15.16	19.43	11.56	19.44
	B	1.640	0.8300	0.176	0.5910	0.3050	0.1760	1.328	0.6170	0.8120	0.5860
	r^2	0.8579	0.9735	0.9384	0.9221	0.9060	0.9916	0.9017	0.9985	0.9471	0.9191
Freundlich	1/n	0.2856	0.0192	0.0607	0.6736	0.0348	0.0369	0.0960	0.0305	0.1818	0.0296
	k_f	0.4709	1.488	0.5657	0.7891	0.5776	1.909	0.8174	1.041	0.8258	0.6693
	r^2	0.9550	0.9614	0.9983	0.9936	0.9861	0.9119	0.9860	0.9994	0.9865	0.9950
Experimental (q_e)		19.07	19.91	15.82	19.95	18.32	19.92	14.50	19.48	11.10	19.94

3.3.1 Temperature Effect Studies

The effect of temperature of the solution (Fig. 10 a–b) from 25 through 80 °C, was evaluated on the adsorption of Pb(II) and methylene blue. Fig. 10 a, showed that temperature increase had a positive effect on UT-BEB and Ac-BEB, it was observed that adsorption of Pb(II) increased with increasing temperature. The plot for Me-BEB showed that as temperature increased from 25 to 30 °C, there was a recorded increase in adsorption however, a further increase in temperature from 30 to 80 °C resulted in reduced adsorption. The recorded increase from 25 to 30 °C was due to little energy required to overcome the repulsive forces hindering Pb(II) adsorption. AA-BEB and DMF-BEB plots recorded a decrease in adsorption of Pb(II) from 25 through 80 °C. Methylene blue plots , showed that Me-BEB and Ac-BEB adsorption increased with increasing temperature. DMF-BEB recorded an increase in adsorption as temperature increased from 25 to 30 °C, thereafter further increase in temperature was detrimental to adsorption. For UT-BEB and AA-BEB temperature increase was detrimental to adsorption from 25 through 80 °C.

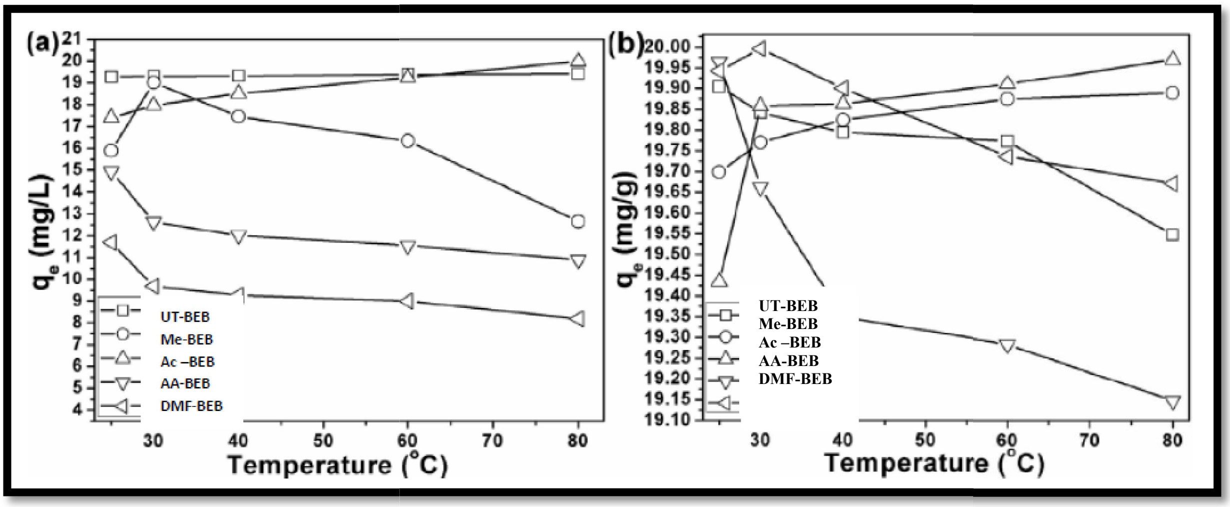

FIGURE. 3 Temperature effect studies of (a) Pb(II) ions and (b) methylene blue adsorption. [Conditions: adsorbent dose (0.1 g), volume (20 ml), pH (5), concentration (100 mg/L) shaking speed (200 rpm), time (120 min)].

3.4. Reusability Studies

The reusability test of UT-BEB, Me-BEB, AA-BEB, Ac-BEB and DMF-BEB was examined in order to establish if black eyed beans adsorbents are economically beneficial. These results showed that the first adsorption cycle recorded the highest adsorption percentage however, the proceeding adsorption cycles slightly decreased in adsorption capabilities. High adsorption in first cycle could be explained by the fact that adsorption sites and pores were abundant on the adsorbents surfaces. Low adsorption in second and third cycles was attributed to the first cycle adsorption process. The adsorbents were unable to desorbs the adsorbed Pb(II) ions and methylene blue within the pores during the regeneration step. Thus, this lowered the second and third adsorption cycles.

3.5 Comparative Study

Table 3 show the adsorption capacities of some of the reported biosorbents in literature compared with black eyed beans. The results show that the adsorption capacities for Pb(II) and methylene blue onto black eyed adsorbents is higher than some biosorbents previously reported. Thus, black eyed beans is a promising cost-effective biosorbent for Pb(II) and methylene blue from aqueous solution.

TABLE 3: Biosorbents comparative study of Pb(II) and methylene blue adsorption.

Biomass adsorbent	***$q_{(max)}$ (mg/g) /Pb(II)***	***References***
Tree fern	30.70	Ho et al. (2004)
Sphagnum moss peat	30.70	Ho et al. (2004)
Untreated black eyed beans	10.96	**This study**
Cashew nut shell	17.80	Kumar (2014)
Formaldehyde modified beans husk	6.410	Adediran et al. (2007)
Pyridine modified beans Husk	1.400	Adediran et al. (2007)
Bean husk	0.9895	husk Onwordi et al. (2019)
Local sourced beans husk	0.3070)	Egwuatu et al. (2013
Biomass adsorbent	***$q_{(max)}$ (mg/g) /Methylene blue***	***References***
Garlic peel	82.60	Hameed and Ahmad et al. (2009)
Methanol treated black eyed	15.56	**This study**

Beans		
Neem leaf powder	19.60	Bhattacharyya and Sharma (2005)
Coconut coir dust	15.25	Kavitha and Namasivayam (2007)
Carbon from hazelnut shell	8.820	Aygun et al. (2003)
Coal fly ash	8.000	Wang et al. (2015)
Apricot stones	4.100	Macedo et al. (2006)
Walnut shells	3.530	Macedo et al. (2006)

IV. CONCLUSION

Characterization of black eyed beans as adsorbents using BET results suggested that it exhibits large pores, which could easily trap Pb(II) ions and methylene blue dye. SEM images revealed that acetone treated black eyed beans (Ac-BEB), methanol treated black eyed beans (Me-BEB) and dimethylformamide treated black eyed beans (DMF-BEB) morphologies were dominated by spherical microstructures. FTIR analysis affirmed the presence of oxygen containing functional groups such as (–OH), (–COOH) and (–C=O) attached to the adsorbents surface. These groups could enhance the adsorption processes. It was found that black eyed beans adsorbents showed higher adsorption capacity for methylene blue dye than Pb(II) ions. Among the studied adsorbents in this work, UT-BEB and Me-BEB showed good adsorption capability for Pb(II) ions and methylene blue respectively. It was also found that the uptake of Pb (II) and methylene blue increased with increase in initial concentration of solution. Temperature increase on the adsorption of Pb(II) had a positive effect on UT-BEB and Ac-BEB. However, this was detrimental for Me-BEB, AA-BEB and DMF-BEB. For methylene blue temperature increase had a positive effect on the adsorption of Me-BEB and Ac-BEB and detrimental for DMF-BEB, UT-BEB and AA BEB. Kinetics studies showed that the adsorption of Pb(II) ions onto AA-BEB and DMF-BEB had good fit for PFO model suggesting that the processes were mainly through weak van der Waals forces. While the rest of the adsorption for Pb(II) and methylene blue found good fit for PSO model indicates that the mechanism involved electrostatic interactions between the pollutants and the binding sites. Thermodynamic parameter (ΔG^o) gave values which were negative for all adsorbents and studied temperatures. This implies that the processes were feasible and spontaneous. Hence black eyed beans were effectively used as adsorbents for the removal of Pb(II) and methylene blue from aqueous solution.