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Adsorption Equilibrium of Pb^{2+} Removal from Aqueous Solutions Using Spent Batteries

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ABSTRACT: The main goals of water treatment at adequate quantity and quality are to improve the living conditions, reduce poverty among the people and to ensure human and economic development. This paper presents a report on removal of lead using a household waste (spent batteries). Spent batteries were collected, sectioned; carbon rods (cathode) were removed washed with distilled water and characterized. Carbon rods were ground into powder and sieved into different particle sizes. Properties of the powdered carbon rods (*PCR*) were studied. Adsorption properties of PCR were studied using synthetic lead solutions, typical raw water and domestic institutional wastewater with a particular attention to its equilibrium isotherms.

The study revealed that PCR has pores, it adsorbed Pb^{2+} from aqueous solutions (synthetic lead solution, raw water and domestic institutional wastewater). Equilibrium isotherms for Pb^{2+} adsorption from aqueous solutions can be grouped into two based on the values of correlation coefficient (R^2) as follows: equilibrium isotherms with $R^2 > 0.95$ (Langmuir, Freundlich, Sips, Langmuir- Freundlich, Crombie-Quilty and McLoughin,Temkin,Koble- Corrigan, Fritz and Schlunder models) and $R^2 < 0.95$ (Hasley and Redlich- Peterson). Applicability of the process to lead ion removal from aqueous solutions showed that *PCR* can be used as an adsorbent for Pb^{2+} ions removal from aqueous solutions.

It was concluded that *PCR* is a good adsorbent for Pb^{2+} ions removal from aqueous solutions.

Keywords: *Spent* batteries, cathode, powdered carbon rods (PCR), adsorption properties, lead removal, equilibrium isotherms

Atık Pilleri Kullanarak Sıvı Çözeltilerden Kaldırılan Pb^{2+}nin Absorbsiyon Denklemi

ÖZET: Yeterli miktar ve kalitede su temin etmenin amaçları, yaşam koşullarını geliştirmek, insanlar arasındaki yoksulluğu (sefaleti) azaltmak, ve insanı ve ekonomik gelişimi garanti altına almaktır. Bu makale, evdeki atık maddeleri (atık pilleri) kullanarak kurşunun giderimi ile ilgili bir rapor sunmaktadır. Kullanılmış piller toplanıldı, bölümlere ayrıldı; katotlar, distile edilmiş suyla yıkandı ve özellikleri belirlendi. Karbon çubuklar, toz haline getirilip, farklı partikül büyüklüğe sahip eleklerden geçirilmiştir. Toz haline getirilmiş karbon çubuklarının (THGKÇ) özellikleri araştırıldı. THGKÇ'nın denge izotermlerine olan ilgiden dolayı; sentetik kurşun çözeltisi, tipik ham su ve yerli kurumsal atık kullanarak THGKÇ'nin absorbsiyon özellikleri incelendi.

Bu çalışmada, gözenekleri olan THGKÇ, sulu çözeltiden (sentetik kurşun çözeltisi, tipik ham su, ve yerli kurumsal atık) Pb^{2+} absorbe edildiği ortaya çıkmıştır. Sulu çözeltisindeki Pb^{2+} absorbsiyonu için korelasyon katsayıları baz alınarak denge izotermleri iki gruba ayrılabilir. Bunlar, $R^2 > 0.95$ (Langmuir, Freundlich, Sips, Langmuir- Freundlich, Crombie-Quilty and McLoughin,Temkin,Koble- Corrigan, Fritz and Schlunder models) ve $R^2 < 0.95$ (Hasley and Redlich- Peterson) şeklinde ifade edilebilir.

Bu çalışmada, sulu çözeltiden kurşun iyonunun giderimi (kaldırılması) ile ilgili bu prosesinin uygulanabilirliği, THGKÇ'nin, sulu çözeltilerden Pb^{2+} iyonlarının giderilmesini sağlayan bir absorbent olabileceğini göstermiştir.

Anahtar Kelimeler: Absorbsiyon özellikleri, atık piller, denge izotermler, katot, kurşun giderimi, THGKÇ

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INTRODUCTION

Metals and their compounds are indispensable to the industrial, agricultural and technological advancement of any nation. The numbers of applications of metals for commercial uses continue to grow with the developments of modern Science and Technology. Inevitably, industrial processes and spent commercial (metallic) products generate large quantity of metallic waste products, which are discharge into the water or land-dump sites. It has been estimated that the toxicity due to metallic discharge annually, into the environments far exceeds the combined total toxicity of all radioactive and organic wastes as measured by the quantity of waste required to dilute such wastes to the drinking water standard (Ismail et al., 2009). This phenomenon gives rise to the growing concern on the gradual build-up of toxic metals such as lead, cadmium, chromium, arsenic etc in the ecosystem. It is well known that Lead in wastewater comes mainly from the discharge of battery manufacturing, printing, dying and other industries (Li et al., 2002). Other major sources of lead in the environment include lead-based paint, household dust and food containers. Lead has been found to be acute toxic to human beings when present in high amounts in water. Studies have shown that young children, infants and pregnant women are particularly susceptible to unsafe lead levels. For adults, increased levels of lead have been linked to high blood pressure and damaged hearing. Drinking, eating, inhaling even at low level of lead can cause other serious health effects.

Lead is a soft highly malleable, bluish-gray metallic element of poor electrical conductor and high resistant to corrosion. Lead (Pb) is used primarily in the storage of batteries, cable covering, plumbing ammunition and in the manufacture of lead tetraethyl (used as an anti-knocking compound in gasoline). It has been in use as a radiation shield from nuclear reactor to X-ray equipment, in glass industries and in paints manufacturing. The most known compounds of lead are galena (PbS), anglesite ($PbSO_4$), cerussite ($PbCO_3$) and minim (Pb_3O_4). Lead contamination of the environment is primarily due to anthropogenic activities making it the most ubiquitous toxic metal in the environment. Research on Pb has become a dominant topic for environmental and medical scientists for two obvious reasons: It has no known biological use and it is toxic to most living things. Lead readily bioaccumulates in the human-rich surface layer of the soils due to its complexation with organic matter. It is the least mobile heavy metal in soils under reducing or non-acidic conditions. Furthermore, it is one of the most common trace metal contaminants in urban soils due to atmospheric deposition from industries and automobile emission. The health effects of lead on man and animals can be summarised as follows: lead is not considered as an essential nutritional element; lead is a cumulative poison to human with typical symptoms as anaemia, constipation, gastrointestinal disturbance, tenderness and gradual paralysis in muscles; it impairment of haemoglobin and porphyrin synthesis; and when Pb is ingested, there is rapid uptake into red blood cells forming PbB, then into soft tissues (kidney, bone marrow, liver and Brain) and followed by a slower redistribution to mineralizing tissues (bones and teeth, Oke et al., 2011).

However, most technologies presently employed for lead removal are based on physicochemical processes, such as dilution, adsorption, coagulation and flocculation, chemical precipitation, oxidation, ion-exchange, reverse osmosis and ultra-filtration. Among these processes, adsorption technology is attractive for the lead treatment from the wastewater, due to its easy availability, simplicity of design, high efficiency, ease of operation, and ability to treat dyes in more concentrated form. Also, lead ions can be removed from solutions by using pH adjustment, chemical treatment, adsorption, electrochemical, ion exchange, precipitation, evaporative recovery, and membrane processes.

Out of all these treatment processes, adsorption has been found economical and applicable at all levels. Also, the main advantage of adsorption is that it is a cheap process with good metal recovery results. Since lead ions can be found in groundwater and surface water (which is the main source of water in rural area of developed and developing countries). It is advisable to study its removal using low cost adsorbents such as powdered corn cobs, other agricultural products and domestic wastes. In previous studies by various researchers various agricultural products and solid wastes have been studied. For examples, leaf mould, activated groundnut husk carbon, coconut husk and palm pressed fibres, coconut shell activated carbon, coconut shell, wood and dust coal activated carbons, coconut jute carbon, coconut tree sawdust carbon, sawdust and used tyres carbon, sawdust, cactus, olive stone/cake, wool, charcoal and pine needles, rice husk carbon, moss, sphagnum moss peat, coconut fibre compost, maize cob, sugar beet pulp and cane bagasse, hazelnut shell activated carbon, almond shell carbon, corncob, quaternized wood, cow dung carbon, waste slurry, iron hydroxide, other materials such as different types of algae, wheat bran, powdered eggshell, and carbon slurry have been reported in literature (Oke et al., 2011). Natural biomasses have been used as adsorbents, either ones that are abundant locally or residual by-products from industrial plants (Oke et al., 2011), algae, bacteria, fungi, higher plants, and products derived from these organisms, have been the potential to remove certain chemicals species.

Also, many reports have appeared on the development of low-cost activated carbon adsorbents developed from cheaper and readily available materials. Khashimova et al. (2008) reported that the use of adsorption for separation of pollutants from mixtures has been increasing continuously and that the main advantages of adsorption are its high selectivity compared with other separation techniques and relatively high capacity of the adsorbents for the pollutants even at low concentrations. The importance of adsorption as water purification process has been documented in literature. Ho (2007) reported that about 9058 articles have been published on adsorption of materials. Figure 1 presents cumulative number of publications, total page counts, number of authors and number of reference cited by year. Activated carbons are widely used as adsorbents because of their high adsorption abilities for a large number of organic compounds (Oke et al., 2011).

However, the price of activated carbons is relatively high, which limits their usage. Biosorption processes, which can be defined as the uptake of contaminants through various physico-chemical mechanisms by inactive/dead biological materials, are relatively easy to operate and posses several inherent advantages, including low cost, operation over a wide range of conditions and possible reuse of biosorbents. Many biosorbent, including bagasse pith, maize cobs, sunflower, peat, orange peel, saw dust, coryne bacterium glutamicum, bentonite, steel-plant slag, fly ash, China clay, waste slurry, and rice husk have been used to remove contaminants from wastewater. In biosorption processes, numerous groups presented that for certain biosorbents, carboxyl, carbonyl, sulphonate, sulphydryl, phosphonate, and hydroxyl groups have proposed to contribute to binding contaminants. These indicate that adsorption process is an important process in environmental pollution control, but adsorption of lead ontopowdered carbon from used dry cells is rare in literature, which calls for documentation of lead adsorption onto this house hold waste considering effects of lead on human's health and on the environment and availability of dry cells as solid waste in developing countries such as Nigeria (Oke, 2007; Oke et al., 2007 a and b); Iran (Zand and Abduli, 2008; Almeida et al., 2009). The main aim of this study was to investigate removal of lead from synthetic water using house hold waste (carbon rods from dry cells, cathode).

MATERIALS AND METHODS

Spent (Used) dry cells (R_{20S} Size D UM-1) were collected from 2002 to 2009 from dustbins, solid waste dump site and street collections. The batteries (dry cells) were characterized, dismantled (sectioned vertically) and the carbon rod (cathode) were removed, washed with distilled water and air dried. The cathodes removed were characterized and ground into powder. Powdered Carbon Rods *(PCR)*were sieved into different particle sizes. Properties of the powdered carbon rods (moisture content, water solubility, acid solubility, ash, and volatile solid and metallic contents) were determined. Structures (micrograph) of the adsorbent were examined to ascertain its nature and porosity. Adsorption properties of the adsorbent were studied using synthetic lead solution and typical wastewaters (raw water and domestic institutional wastewater) with a particular attention to equilibrium isotherms. Environmental economics analysis of *PCR* processing was conducted based on literature. *PCR* was selected based on availability in developing countries as solid wastes.

Moisture content: A well mixed samples of PCR were evaporated in a weighed dishes to a constant weight in an oven at 105°C (APHA, 1998). In detail, the samples were weighed initially, dried in the oven at 105 °C for 24 hours, cooled in desiccators and reweighed. The decreased in the weight of the PCR represents the moisture content as follows:

$$M_c(\%) = 100\left(\frac{W_1 - W_2}{W_1}\right) \tag{1}$$

Volatile Solid And Ash Content: Known masses of dried samples used for moisture content determination were placed in crucible dishes and transferred into a muffle furnace. The furnace was heated to 550°C for 2 hours (APHA, 1998). The samples were cooled in desiccators to balance the temperature and the final weights were measured. Volatile solid and ash content of PCR were calculated as follows (APHA, 1998):

$$VS\,(\%) = 100\left(\frac{W_2 - W_3}{W_2}\right) \tag{2}$$

$$Ash\,(\%) = 100\left(\frac{W_3}{W_1}\right) \tag{3}$$

Water and acid solubilities: Known dried masses of the samples were soaked in 300 ml of distilled water and in 300 ml of 0.25 M of HCl (hydrochloric acid) for 24 hours respectively. The samples were filtered out using pre-dried and weighted filter paper (Number 1). The samples and the filter paper were dried in the oven at 105^{o}C for 24 hours, cooled in desiccators to balance the temperature and the final weights were measured. Water and acid solubilities of PCR were calculated as follows (APHA, 1998):

$$WS(\%) = 100\left(\frac{W_2 - W_4}{W_2}\right) \tag{4}$$

$$AS\,(\%) = 100\left(\frac{W_2 - W_5}{W_2}\right) \tag{5}$$

Metal concentrations: A known mass of the PCR was digested using nitric acid digestion method (APHA, 1998) and chemical components of the adsorbent were determined using standard methods (APHA, 1998). Specifically, 1.0 gram of PCR was digested using nitric acid and total metal concentrations were determined using spectormetry method. Metal concentrations were computed as follows:

$$M_{cc}\,(mg/L) = \left(\frac{A * B}{W_1}\right) \tag{6}$$

In the preparations of lead solutions, procedures specified in Standard Methods for the Examination of Water and Wastewater (APHA, 1998) were followed. Specifically a known mass (1.599g) of lead nitrate ($Pb(NO_3)_2$) was dissolved in 200 ml of distilled water, 10 ml of concentrated trioxonitrate (V) acid (*HNO_3)* was added, diluted to 1000ml mark using distilled water and working solutions were prepared from the stock solution. In the determination of adsorption capacities, 300 ml of the lead solutions containing a known concentration (mg/L) of Pb^{2+} were taken into five different beakers and known masses (0.3, 0.5, 0.7, 1.0 and 1.2g) of the adsorbent were added at a known initial pH. The mixture was stirred at 60 revolutions per minute (rpm) for 2 minutes and allowed to settle for 18 hours (when equilibrium concentrations have been reached). The supernatant of the samples taken were filtered through Whatman filter paper number 40 to prevent particulate. Determinations of lead concentrations were conducted using spectrophotometer method (APHA, 1998) and spectrophotometer facilities available at Central Science Laboratory ObafemiAwolowoUniversity, Ile-Ife, Nigeria. Equilibrium and kinetics parameters and percentage lead adsorbed were computed by using equations (7 and 8) as follows:

$$q_e = \frac{(C_0 - C_e)}{M} V \tag{7}$$

$$R_R(\%) = 100\frac{(C_0 - C_t)}{C_0} \tag{8}$$

Effects of pH, initial Pb^{2+} concentration and particle size of the PCR on adsorption properties were studied.

RESULTS AND DISCUSSION

The results of this study have been presented and discussed in the following ways: types of spent batteries collected characterization of the cathode, selected properties of *PCR* and adsorption properties (equilibrium models) of Pb^{2+}onto *PCR*. Comparison between the result and other results from literature.

TypesofSpentBatteries: Figure 2 (a and b) presents various R_{20S} Size D UM-1 batteries collected. Out of about 150, 000 spent batteries collected the orders of their numbers are as follows: Tiger > flash >XionJian>Berec (England and Nigeria) > Duracell > Tudor > others. Figure 2(c_i and c_{ii}) presents vertical section (dismantled) batteries as presented in another paper (Oke et al., 2010).

Characterisation Of The Cathode : Table 1 presents physical properties and chemical composition of the cathode. From the table it can be seen that it contains no cadmium (Cd), arsenic (As), chromium (Cr) chloride (Cl^-), sulphate (SO_4^{2-}), lead (Pb^2+), manganese

(Mn) and zinc (Zn). This indicates that utilization of PCR as an adsorbent cannot impose any danger or harm on the environment and human's health rather it will help in cleaning the environment as follows:

Removal of Pb^{2+} by PCR (as it is known that lead is toxic and harmful to man);

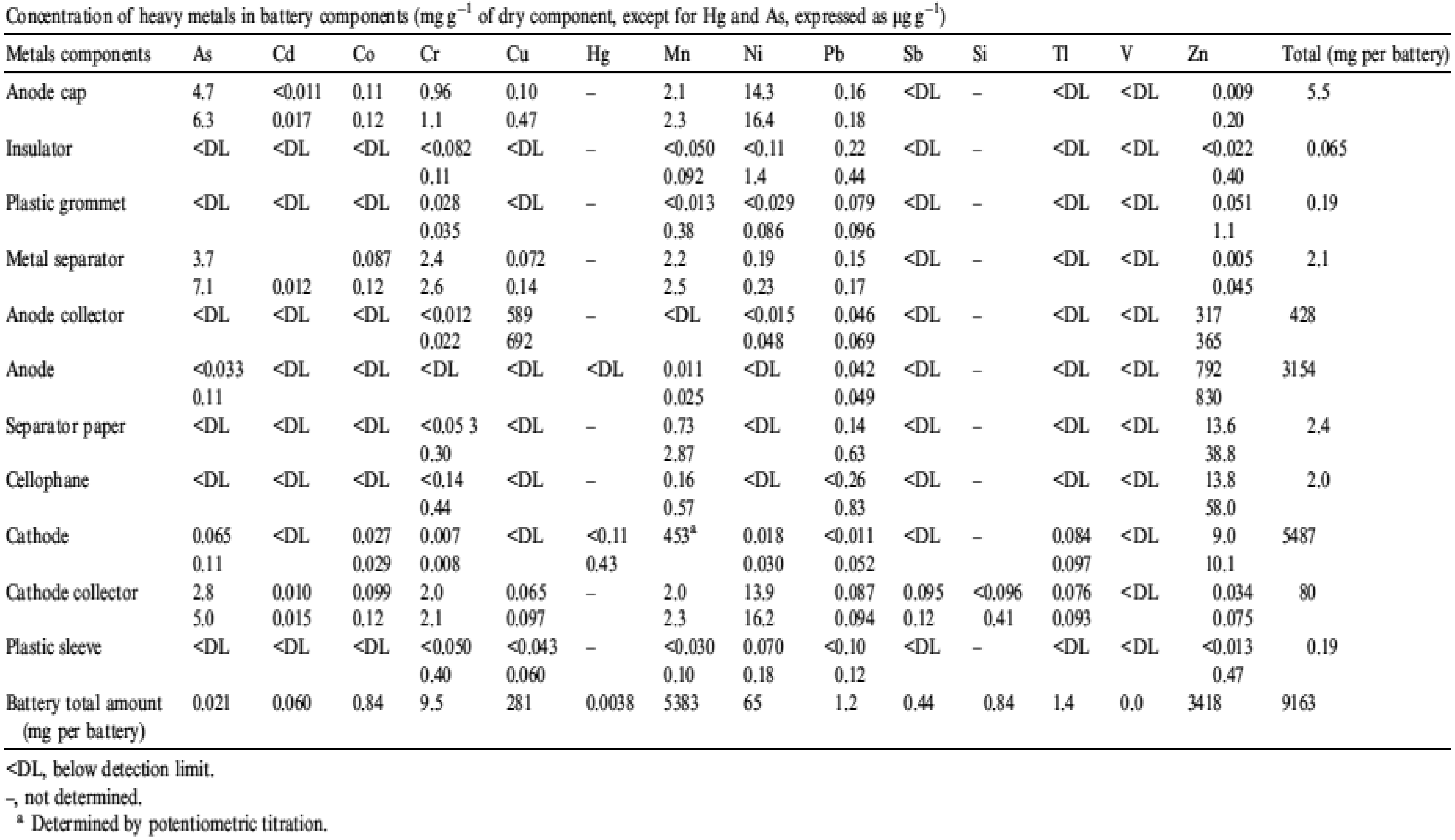
Removal of spent batteries reduces solid wastes disposal problem as in developing countries there is no law against disposing the waste in the municipal waste. Figure 3 presents environmental economic analysis of spent batteries removal from the environment. Literature such as Almeida et al (2006) present properties of AA household alkaline batteries [Table 1 (a)]

Properties of PCR: Figures 4 - 9 present micrographs of the *PCR* of different particle size recorded at same magnification of using Accu-scope microscope of 0524011 model. The Micrographs clearly revealed the surface texture and porosity of the adsorbent with holes and small openings found on the surface indicating that it would increase the contact area and facilitate pore diffusion during adsorption. Availability of these pores (opens) makes it possible for *PCR* to accommodate Pb^{2+} through settlement of the pollutants on *PCR*. Literature such as Wu et al (2006) provides SEM of graphite (Figure 10 presents SEM as obtained from literature).

Table 1. Selected properties of carbon rods and powdered carbon rods

Property	Mean	Maximum	Minimum	Standard Deviation
Ash (%)	99.78	99.82	99.77	0.02
Volatile Solids (%)	0.22	0.23	0.18	0.02
Moisture content (%)	0.25	0.26	0.25	0.00
Water Solubility (%)	3.43	3.49	3.37	0.05
Acid Solubility (%)	5.98	6.09	5.87	0.08
Density (g/cm^3)	1.48	1.50	1.45	0.02
Mass (g)	5.53	5.63	5.43	0.08
Sulphate(mg/g)	0.00	0.00	0.00	0.00
Chloride (mg/g)	0.00	0.00	0.00	0.00
As (mg/g)	0.00	0.00	0.00	0.00
Cd (mg/g)	0.00	0.00	0.00	0.00
Chromium (mg/g)	0.00	0.00	0.00	0.00
Copper (mg/g)	0.00	0.00	0.00	0.00
Lead (mg/g)	0.00	0.00	0.00	0.00
Manganese (mg/g)	0.01	0.01	0.01	0.00
Zinc (mg/g)	0.05	0.05	0.05	0.00

Table 1(a). Concentration of heavy metals in battery components (mg g^{-1} of dry component, except for Hg and As, expressed as µgg^{-1})
(Source: Almeida et al., 2006)



Concentration of heavy metals in battery components (mg g^{-1} of dry component, except for Hg and As, expressed as µg g^{-1})

Metals components	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Sb	Si	Tl	V	Zn	Total (mg per battery)
Anode cap	4.7	<0.011	0.11	0.96	0.10	–	2.1	14.3	0.16	<DL	–	<DL	<DL	0.009	5.5
	6.3	0.017	0.12	1.1	0.47		2.3	16.4	0.18					0.20	
Insulator	<DL	<DL	<DL	<0.082	<DL	–	<0.050	<0.11	0.22	<DL	–	<DL	<DL	<0.022	0.065
				0.11			0.092	1.4	0.44					0.40	
Plastic grommet	<DL	<DL	<DL	0.028	<DL	–	<0.013	<0.029	0.079	<DL	–	<DL	<DL	0.051	0.19
				0.035			0.38	0.086	0.096					1.1	
Metal separator	3.7		0.087	2.4	0.072	–	2.2	0.19	0.15	<DL	–	<DL	<DL	0.005	2.1
	7.1	0.012	0.12	2.6	0.14		2.5	0.23	0.17					0.045	
Anode collector	<DL	<DL	<DL	<0.012	589	–	<DL	<0.015	0.046	<DL	–	<DL	<DL	317	428
				0.022	692			0.048	0.069					365	
Anode	<0.033	<DL	<DL	<DL	<DL	<DL	0.011	<DL	0.042	<DL	–	<DL	<DL	792	3154
	0.11						0.025		0.049					830	
Separator paper	<DL	<DL	<DL	<0.05 3	<DL	–	0.73	<DL	0.14	<DL	–	<DL	<DL	13.6	2.4
				0.30			2.87		0.63					38.8	
Cellophane	<DL	<DL	<DL	<0.14	<DL	–	0.16	<DL	<0.26	<DL	–	<DL	<DL	13.8	2.0
				0.44			0.57		0.83					58.0	
Cathode	0.065	<DL	0.027	0.007	<DL	<0.11	453^{a}	0.018	<0.011	<DL	–	0.084	<DL	9.0	5487
	0.11		0.029	0.008		0.43		0.030	0.052			0.097		10.1	
Cathode collector	2.8	0.010	0.099	2.0	0.065	–	2.0	13.9	0.087	0.095	<0.096	0.076	<DL	0.034	80
	5.0	0.015	0.12	2.1	0.097		2.3	16.2	0.094	0.12	0.41	0.093		0.075	
Plastic sleeve	<DL	<DL	<DL	<0.050	<0.043	–	<0.030	0.070	<0.10	<DL	–	<DL	<DL	<0.013	0.19
				0.40	0.060		0.10	0.18	0.12					0.47	
Battery total amount (mg per battery)	0.021	0.060	0.84	9.5	281	0.0038	5383	65	1.2	0.44	0.84	1.4	0.0	3418	9163

<DL, below detection limit.
–, not determined.
^{a} Determined by potentiometric titration.

Adsorptionproperties (equilibriummodels) of Pb^{2+}onto PCR: Adsorption properties can be expressed in two ways as equilibrium isotherms and kinetics models.

Equilibrium is otherm models: It is well known that isotherm data are basic requirements for the design of adsorption reactors and analysis of adsorption isotherm is an important thing in environmental pollution control. The key thing is to develop an equation which will accurately represent the results and which can be used for design purposes (Aksu, 2002). This information can be used to study the adsorption kinetics of a single component, adsorption equilibria of multicomponent systems, and adsorption kinetics of multicomponent systems. There are many basic adsorption equilibrium isotherm models, which include: Langmuir, Freundlich, Crombie-Quilty and McLoughin (activated sludge), BET, Nerst and activated sludge isotherms (Oke et al., 2008), Temkin and Redlich- Peterson isotherms (Otun et al., 2006 (a) and (b); Ho and Mckay, 1998(a) and(b), Gile's classification isotherms (Esmaili et al., 2005), Toth (Toth, 1983) ; Dubinin–Radushkevich (Nameni et al., 2008); Khan (Kim et al., 2002); Fritz and Schlunder (Kim et al., 2002) . Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, (Nameni et al., 2008*);* Sips, Radke-Prausnitz (Olarinoye et al., 2011), ideal adsorbed solution theory *(IAST)* and Redlich-Peterson isotherms are some of the isotherms that are commonly used in engineering applications. Literature such as Hwang et al., (1991); Moon et al., (1989); Myers and Prausnitz (1965) provides information on IAST and on vacancy solution theory *(VST*). Table 2 shows various adsorption equilibrium isotherms for single component solutions.

Langmuir model: Langmuir isotherm is physically plausible isotherm, which was developed from a theoretical consideration, which is based on three assumptions, namely: adsorption cannot proceed beyond monolayer coverage, all surface sites are equivalent and can accommodate at most one adsorbed atom; and the ability of a molecule to adsorb at a given site is independent of the occupation of neighbouring sites. At equilibrium there is no net change of surface coverage, the rate of change of concentration due to adsorption should be equal to the rate of change of concentration due to desorption. As a result the Langmuir isotherm is expressed as (Oke et al, 2008):

$$q_e = \frac{a_L b_L C_e}{1 + a_L C_e} \tag{9}$$

Rearranging equation (9) to give equations (10 and 11) make the equation to be linearised, from which the values of a and b can be determined from slope and intercept respectively.

$$\frac{1}{q_e} = \frac{1 + a_L C_e}{a_L b_L C_e} \tag{10}$$

$$\frac{1}{q_e} = \frac{1}{b_L} + \frac{1}{a_L b_L}\frac{1}{C_e} \tag{11}$$

Table 3 shows results of the adsorption capacity analysis of Pb^{2+} onto PCR using equilibrium models. The estimated adsorption parameters by the Langmuir model are shown in Table 3 (Figure 11a). The values of Langmuir constants a_L and b_L (0.276 L/ mg and 6.039 mg/mg respectively) and the squared of regression coefficient ($R^2 = 0.964$) suggested that the adsorption of lead ion onto PCR can be modelled by the Langmuir isotherm. The value of b_L indicates that PCR as an adsorbent that would be effective when initial concentrations of lead ion are high. It (b_L) relates adsorption of lead ion to the sorption potential of the PCR. Also, the value of $b_L$shows that with an increase in PCR dose, the equilibrium adsorption capacity,(q_e), will decrease [Adie et al., 2010]. These values of parameters (a_L and b_L) were lower than the values obtained for HSAC at pH of 1, 1.5, 2.0 and 3 but higher than values at pH of 6 and 8, which indicate that PCR is a valuable adsorbent as HSAC (hazenut shell activated carbon). Also, the value of adsorption capacities were higher than adsorption capacities of some materials such as china clay, coke, spruce sawdust, illite clay, soil kaolinite clay and linden saw dust (Table 4). Furthermore, the value of b_L revealed that 6.039mg of lead ion was removed by 1.00 gram of PCR. This adsorption value indicates that adsorption of lead ion onto PCR was not only based on physical adsorption but involved flocs formation and charges attraction (involved both chemical and physical adsorptions). Applicability of the technique on raw water and domestic institutional samples revealed that the technique is applicable with Langmuir parameters (b_L and a_L) found to be 5.461 mg/g (that is 5.461mg of lead ion was removed by 1.0g of PCR from raw waterand 22.779 mg/g, that is 22.779 mg of lead ion was removed by 1.0g of PCR from domestic institutional wastewater which are known to be multi-component systems), and 0.278 L/mg and 0.076 L/mg respectively. Although, the values for raw water were lower than expected values (from synthesis Pb^{2+} aqueous solution), this might be attributed to heterogenic nature of the raw water. These results revealed that PCR as an adsorbent that will be applicable in the separation of pollutants from aqueous solutions as it is known that adsorption processes in wastewater treatment and water treatment plants as well as in the aquatic environment take place in multi-components (Adie et al., 2010).

It has been well documented that the essential characteristic of the Langmuir isotherm may be expressed in terms of the dimensionless parameter (R_L). R_L has been defined as the isotherm shape that predicts if an adsorption system is favourable or unfavourable. Literature (Adie et al., 2010; Oke et al., 2008) states that R_L indicates the isotherm shape according to the following adsorption characteristics, $R_L > 1$ (is unfavourable), $R_L = 1$ (linear adsorption), $R_L = 0$ (is irreversible) and $0 < R_L < 1$ (is favourable) It has been expressed as follows:

$$R_L = \frac{1}{1 + b_L C_0} \tag{12}$$

For lead ion adsorption onto PCR the value of R_L was found to be 0.014; 0.268 and 0.049 ($0 < R_L < 1$) for synthetic wastewater, raw water and domestic-institutional wastewater respectively. These values of R_L indicate that adsorption of lead on PCR is favourable (Adie et al., 2010), but the adsorption will be influenced by higher initial lead ion concentrations and adsorption capacities may increases at higher adsorbent mass .

Freundlich Model: The Freundlich isotherm is an empirical relationship, which often gives a more satisfactory model of experimental data (Oke et al., 2008). It can be expressed as shown in equation (13). Figure 12 (a, b and c) showsFreundlich model of the adsorption, while Table 3 presents values isotherm parameters by Freundlich model.

$$q_e = K_f C_e^{1/N_f} \tag{13}$$

From figures it can be seen that non-linear relationship was used, this was done based on literature (Ho, 2006). From the figures the values of K_f and N_f (Freundlich constants) can be obtained by plotting adsorption capacities against equilibrium concentration. The estimated adsorption parameters by the Freundlich model are as shown in Figure 12. The values of K_f (1.486, 5.051 and 0.914 mg/g) and$N_f$values (0.393, 0.936 and 1.926 L/mg) from the Freundlich isotherm (Figure 12) suggests that the adsorption capacities of PCR were high and that any large change in the equilibrium concentration of lead ion would not result in a remarked change in the amount of lead ion adsorbed by PCR. The correlation coefficients (R^2) for Freundlich isotherm are 0.999, 0.999 and 0.956 for synthetic, raw water and domestic institutional wastewater representing goodness of fits of the observed data. These high squared correlation coefficients confirm literature on Freundlich isotherm (Oke et al., 2008). The values of K_f and N_f were different from the values documented in Mamdouth et al (2004) and in Kobya (2004), which indicate that adsorption onto materials with carbon or agricultural materials is different from adsorption onto PCR and adsorption capacities is a function of the material used and its components. Figures 13, 14 and 15 present relationships between pH and Freundlich isotherm parameters, particle size and Freundlich parameters, initial lead concentration and Freundlich parameters respectively.A study on effects of, pH, particle sizes and initial Pb^{2+} concentration on the adsorption capacities revealed that adsorption of Pb^{2+} onto PCR depends on particle size of PCR and initial concentration of lead ion (Figures 13, 14 and 15). These phenomena can be attributed to increases surface area and availability of charged pore.

Crombie-Quilty and McLoughin model: Oke et al (2008) reported that the Crombie-Quilty and McLoughin isotherm was developed by Crombie-Quilty and McLoughin, the model describes floc formation at an equilibrium concentration. The model (Crombie-Quilty and McLoughin model) is known as activated sludge model. The activated adsorption equation is as shown in equation (14).

$$q_e = K_m \left(\frac{C_e}{M} \right)^{\frac{1}{N_m}} \tag{14}$$

Like Freundlich isotherm model, non-linear relationship was used based on the same reason. From the figure the values of K_m and N_m were obtained by plotting adsorption capacities against equilibrium concentrations. The estimated adsorption parameters by the activated adsorption model are as shown in Figure 16 (a, b and c) and Table 3. A low level of K_m (4292.30) from the activated sludge isotherm suggests that the tendency of floc formation during adsorption is possible but at a higher rate. A higher $1/N_m$value of 1.111 (greater than 1) from the activated sludge isotherm suggests that any large change in the equilibrium concentration of lead ion would result in a change in the amount of lead ion floc formation by PCR. The squared correlation coefficient (R^2) for activated sludge isotherms (0.969) also represents an excellent fitness of the observed data for synthetic wastewater. The test for applicability revealed that the technique is applicable with Crombie-Quilty and McLoughin parameters (K_m and N_m) were found to be 22.287 mg/g and 2.198L/mg, and 0.253 mg/g and 1.435 L/mg for raw water and domestic institutional wastewater respectively.

Hasley model: Literature reported that the Hasley isotherm was developed by Hasley, the model describes floc formation at an equilibrium concentration. The Hasley adsorption equation is as shown in equation (15).

$$q_e = \left(\frac{K_H}{C_e}\right)^{\frac{1}{N_H}} \tag{15}$$

Like Freundlich, Crombie-Quilty and McLoughin isotherm models, non-linear relationship was used based on the same reason. From the figure the values of K_H and N_H were obtained by plotting adsorption capacities against equilibrium concentrations. The estimated adsorption parameters by the activated adsorption model are as shown in Figure 17 (a, b and c) and Table 3. A high level of K_H (15.55)from the Hasley isotherm suggests that the tendency of floc formation during adsorption is possible but at a higher rate. A higher $1/N_H$value of 0.125 (less than 1) from the Hasley isotherm suggests that any large change in the equilibrium concentration of lead ion would result in a change in the amount of lead ion floc formation by PCR. The squared correlation coefficient (R^2) for Hasley isotherms (0.845) also represents an average fitness of the observed data for synthetic wastewater. The test for applicability revealed that the technique is applicable with Hasley parameters (K_m and N_m) were found to be 6.580 mg/mg and 14.577 L/mg, and 0.552 mg/mg and 13.62 L/mg with R^2 of 0.999 and 0.795 for raw water and domestic institutional wastewater respectively. These results disagree with literature on comment on Hasley isotherm model.

The Temkin isotherm model: The Temkin isotherm model is an empirical relationship, which often gives a more satisfactory model of experimental data (Adie et al., 2010). It can be expressed as shown in equation (16). Figure 18 (a, b and c) shows Temkin isotherm model of the adsorptions.

$$q_e = a_t + 2.3b_t \log C_e \tag{16}$$

From the figure, the values of a_t and b_t (Temkin's constants) were obtained by plotting of adsorption capacities against equilibrium concentrations. Estimated adsorption parameters by the Temkin model are as shown in Figure 18 (Table 3). The values of a_t (3.685L/mg) and b_t (18.853 mg/g) from the Temkin isotherm suggests that the adsorption capacity of PCR was high and that any large change in the equilibrium concentration of Pb^{2+} ions would not result in a marked change in the amount of Pb^{2+} ions adsorbed by PCR. The squared correlation coefficients (R^2) for Temkin isotherm is 0.967 representing a good fitness ($R^2 > 0.95$) of the observed data [Adie et al., 2010; Ismail et al., 2009]. This high squared correlation coefficient indicates that Temkin isotherm model can be used to model adsorption of Pb^{2+} ions onto PCR correctly. The values of R^2, a_t and b_t were different from the values documented in literature such as Otun et al [2006b], which indicate that adsorption of Pb^{2+} PCR can be model by Temkin equation like adsorption of lead ion onto synthetic hydrous stannic oxide, unlike Pb^{2+} unto PCC (Ismail et al., 2009). Figure 18 (b and c) presents the parameters by Temkin model using raw water and domestic institutional wastewater samples respectively.

The disadvantage of the Freundlich model is that it does not reduce to Henry's law as the concentration approaches zero. Redlich–Peterson, Sips, Langmuir-Freundlich, Koble- Corrigan and Fritz- Schhundler modelsfulfil this condition. These models have a linear dependence on concentration in the numerator and an exponential function in the denominator. It may be represented by the equations (17 - 21) as follows:

$$q_e = \frac{a_t C_e}{1 + b_t C_e^g} \qquad (17)$$

$$q_e = \frac{a_{ts} C_e^{g_{ts}}}{1 + \beta_{tb} C_e^{g_{ts}}} \qquad (18)$$

$$q_e = \frac{q_m K_t C_e^{K_{LF}}}{1 + K_t C_e^{K_{LF}}} \qquad (19)$$

$$q_e = \frac{a_{kc} C_e^{g_{kc}}}{\left(1 + b_{kc} C_e^{g_{kc}}\right)} \qquad (20)$$

$$q_e = \frac{q_{mfs} \alpha_{fs} C_e^{\gamma_{fst}}}{\left(1 + \alpha_{fs} C_e^{\gamma_{fst}}\right)} \qquad (21)$$

The Redlich- Peterson isotherm is an empirical relationship, which often gives a more satisfactory model of experimental data. Figure 19 (a, b and c) and Table 3 show Redlich- Peterson model of the adsorption and their values respectively.

$$q_e = \frac{\alpha_t C_e}{1 + \beta_t C_e^{\gamma}} \qquad (17)$$

For $\beta_t = 1$, the equation converts to the Langmuir isotherm; for $1 >> \beta_t C^{\gamma}_e$ it simplifies to Henry's law; and for $1 << \beta_t C^{\gamma}_e$ it is identical with the Freundlich isotherm. The linear form is given in equation (17a) from which the constants α_t, γ and β_t which characterized the isotherm can be determined.

$$\frac{C_e}{q_e} = \frac{1}{\alpha_t} + \frac{\beta_t}{\alpha_t} C_e^{\gamma} \qquad (17a)$$

Plotting ratio of equilibrium concentration and equilibrium parameter on the left hand side against equilibrium concentrations the unknown parameters were found (Figure 19). From the figure the values of α_t, γ and β_t were obtained. The estimated adsorption parameters for the Redlich- Peterson model are shown in Figure 19 and Table 3. The values of α_t(1.451 L/mg); γ (0.634mg/g) and β_t (0.140mg/g) by the Redlich- Peterson isotherm for synthetic wastewaters, α_t(4.184 L/mg); γ (0.086mg/g) and β_t (1.247mg/g) for raw water and α_t(17.057 L/mg); γ (0.353 mg/g) and β_t (15.157 mg/g) for domestic institutional wastewater suggest that the adsorption capacity of PCR was high and that any large change in the equilibrium concentration of Pb^{2+} ions would not result in a remarked change in the amount of Pb^{2+} ions adsorbed by PCR. The squared correlation coefficients (R^2) for Redlich- Peterson isotherm are 0.822, 0.818 and 0.839 for synthetic wastewater, raw water and domestic institutional wastewater respectively. These values of R^2 represent media fitness ($0.75 < R^2 < 0.95$) of the observed data for adsorption Pb^{2+} ions adsorption onto PCR. The value of α_t and β_t for this model are different from the values documented in literature such as Mamdouth et al [2004], Oke et al [2008] and in Kobya [2004], which indicate that adsorption onto carbon is different from adsorption onto PCC and PES.

The Sips, Koble- Corrigan, Fritz- Schhundler or Langmuir- Freundlich isotherm also contains three parameters like Redlich- Peterson isotherm. The Sips isotherm can be represented as

$$q_e = \frac{\alpha_{ts} C_e^{\gamma_{ts}}}{1 + \beta_{ts} C_e^{\gamma_{ts}}} \qquad (18)$$

Like Redlich- Peterson isotherm model, for $\beta_{ts} = 1$, the equation converts to the Langmuir isotherm; for $1 >> \beta_{ts} C^{\gamma}_{tse}$ it simplifies to Henry's law; and for $1 << \beta_{ts} C^{\gamma}_e$ it is identical with the Freundlich isotherm. The linear form is given in equation (18a) from which the constants α_{ts}, γ_{ts} and β_{ts} which characterized the isotherm can be determined.

$$\frac{1}{q_e} = \left(\frac{1}{a_{ts}}\right)\left(\frac{1}{C_e^{g_{ts}}}\right) + \frac{b_{ts}}{a_{ts}} \qquad (18a)$$

Plotting ratio of equilibrium concentration and equilibrium parameter on the left hand side against equilibrium concentrations the unknown parameters were found (Figure 20). From the figure the values of α_t, γ and β_t were obtained. The estimated adsorption parameters for the Redlich- Peterson model are shown in Figure 20 and Table 3. The values of α_{ts}(1.445 L/mg); γ_{ts} (2.576mg/g) and β_{ts} (0.036mg/g) by the Sips isotherm for synthetic wastewaters, α_{ts}(4.810 L/mg); γ_{ts} (0.967mg/g) and β_{ts} (0.108mg/g) for raw water and α_{ts}(2.974 L/mg); γ_{ts} (1.376 mg/g) and β_{ts} (0.045 mg/g) for domestic institutional wastewater suggest that the adsorption capacity of PCR was high and that any large change in the equilibrium concentration of Pb^{2+} ions would not result in a remarked change in the amount of Pb^{2+} ions adsorbed by PCR. The squared correlation coefficients (R^2) for Sips isotherm are 0.988, 0.962 and 0.956 for synthetic wastewater, raw water and domestic institutional wastewater respectively. These values of R^2 represent high fitness ($R^2 > 0.95$) of the observed data for adsorption Pb^{2+} ions adsorption onto PCR.

The Koble- Corrigan isotherm can be represented as

$$q_e = \frac{\alpha_{kc} C_e^{\gamma_{kc}}}{\left(1 + \beta_{kc} C_e^{\gamma_{kc}}\right)} \qquad (20)$$

Like other three parameters models, for $\beta_{kc} = 1$, the equation converts to the Langmuir isotherm; for $1 >> \beta_{kc} C^{\gamma}_{kc\,e}$ it simplifies to Henry's law; and for $1 << \beta_{kc} C^{\gamma}_{e}$ it is identical with the Freundlich isotherm. The linear form is given in equation (20a) from which the constants $\alpha_{kc\,t}$, γ_{kc} and β_{kc} which characterized the isotherm can be determined.

$$\frac{1}{q_e} = \left(\frac{1}{\alpha_{kc}}\right)\left(\frac{1}{C_e^{\gamma_{kc}}}\right) + \frac{\beta_{kc}}{\alpha_{kc}} \qquad (20a)$$

Plotting equilibrium parameter on the left hand side against equilibrium concentrations the unknown parameters were found (Figure 14). From the figure the values of α_{kc}, γ_{kc} and β_{kc} were obtained. The estimated adsorption parameters for the Koble- Corrigan model are shown in Figure 21 and Table 3. The values of α_{kc} (1.445 L/mg); γ_{kc} (2.576mg/g) and β_{kc} (0.036mg/g) by the Koble- Corrigan isotherm for synthetic wastewaters, α_{kc} (4.810 L/mg); γ_{kc} (0.967mg/g) and β_{kc} (0.108mg/g) for raw water and α_{kc} (2.974 L/mg); γ_{kc} (1.376 mg/g) and β_{kc} (0.045 mg/g) for domestic institutional wastewater suggest that the adsorption capacity of PCR was high and that any large change in the equilibrium concentration of Pb^{2+} ions would not result in a remarked change in the amount of Pb^{2+} ions adsorbed by PCR. The squared correlation coefficients (R^2) for Koble- Corrigan isotherm are 0.988, 0.962 and 0.956 for synthetic wastewater, raw water and domestic institutional wastewater respectively. These values of R^2 represent media fitness ($R^2 > 0.95$) of the observed data for adsorption Pb^{2+} ions adsorption onto PCR.

The Fritz- Schhundler isotherm can be represented as

$$q_e = \frac{q_{mfs} \alpha_{fs} C_e^{\gamma_{fst}}}{\left(1 + \alpha_{fs} C_e^{\gamma_{fst}}\right)} \qquad (21)$$

Like other three parameters, for $\alpha_{fst} = 1$, the equation converts to the Langmuir isotherm; for $1 >> \alpha_{fst} C^{\gamma}_{e}$ it simplifies to Henry's law; and for $1 << \alpha_{fst} C^{\gamma}_{e}$ it is identical with the Freundlich isotherm. The linear form is given in equation (21a) from which the constants α_{fst}, γ_{fst} and q_{mfs} which characterized the isotherm can be determined.

$$\frac{1}{q_e} = \left(\frac{1}{q_{mfs}\alpha_{fs}}\right)\left(\frac{1}{C_e^{\gamma_{fst}}}\right) + \frac{1}{q_{mfs}} \qquad (21a)$$

Plotting ratio of inverse of equilibrium concentration and equilibrium parameter on the left hand side against equilibrium concentrations the unknown parameters were found (Figure 22). From the figure the values of α_{fst}, γ_{fst} and q_{mfs} were obtained. The estimated adsorption parameters for the Fritz- Schhundlermodel are shown in Figure 22 and Table 3. The values of q_{mfs} (0.728 mg/g); γ_{fst} (2.542 mg/g) and α_{fs} (2.045 L/mg) by the Fritz- Schhundler isotherm for synthetic wastewaters, q_{mfs} (2.165 mg/g); γ_{fst} (1.086 mg/g) and α_{fs} (2.410 L/mg) for raw water and q_{mfs} (0.734 mg/g); γ_{fst} (0.716 mg/g) and α_{fs} (1.776 L/mg) for domestic institutional wastewater suggest that the adsorption capacity of PCR was high and that any large change in the equilibrium concentration of Pb^{2+} ions would not result in a remarked change in the amount of Pb^{2+} ions adsorbed by PCR. The squared correlation coefficients (R^2) for Fritz- Schhundler isothermare 0.999, 0.999 and 0.945 for synthetic wastewater, raw water and domestic institutional wastewater respectively. These values of R^2 represent good fitness ($R^2 > 0.95$) of the observed data for adsorption Pb^{2+} ions adsorption onto PCR.

The Langmuir- Freundlich isotherm can be represented as

$$q_e = \frac{q_m K_t C_e^{K_{LF}}}{1 + K_t C_e^{K_{LF}}} \qquad (22)$$

For $K_t = 1$, the equation converts to the Langmuir isotherm; for $1 >> K_t C^{KLF}_{e}$ it simplifies to Henry's law; and for $1 << K_t C^{KLF}_{e}$ it is identical with the Freundlich

Table 2. Adsorption equilibrium isotherm for single component aqueous solutions (Source: Oke et al., 2011)

Type	Relationship	Parameters
Langmuir	$q_e = \frac{a_L b_L C_e}{1 + a_L C_e}$	a_L and b_L
Freundlich	$q_e = K_f C_e^{1/N_f}$	K_f and N_f
Redlich–Peterson	$q_e = \frac{\alpha_t C_e}{1 + \beta_t C_e^{\gamma}}$	α_t, γ and β_t
Temkin	$q_e = a_t + 2.3 b_t \log C_e$	a_t and b_t
Crombie-Quilty and McLoughin	$q_e = K_m \left(\frac{C_e}{M} \right)^{1/N_m}$	K_m and N_m
Sips	$q_e = \frac{\alpha_{ts} C_e^{\gamma\, ts}}{1 + \beta_{ts}\, C_e^{\gamma\, ts}}$	α_{ts}, γ_{ts} and β_{ts}
Langmuir- Freundlich	$q_e = \frac{q_m K_t C_e^{K_{LF}}}{1 + K_t C_e^{K_{LF}}}$	q_m, K_{LF} and K_t
Toth	$q_e = \frac{q_m \alpha_{tt}{}^{g_t} C_e}{\left(1 + \alpha_{tt} C_e^{\gamma\, tt}\right)^{\left(\frac{1}{\gamma_t}\right)}}$	q_m, $\alpha_{tt,}$ and γ_{tt}
	$q_e = \frac{a_t C_e}{\left(b_t + C_e^{g_t}\right)^{\left(\frac{1}{g_{tt}}\right)}}$	$\alpha_{tt,}$ β_{tt} and γ_{tt}
Radke-Prausnitz	$\frac{1}{q_e} = \left(\frac{\alpha_{rp}}{C_e}\right) + \frac{\beta_{rp}}{\left(C_e^{\gamma\, rp}\right)}$	α_{rp}, $\gamma_{rp}$and β_{rp}
	$q_e = \frac{q_m \alpha_{rp} C_e}{\left(1 + \alpha_{rp} C_e^{\gamma\, tt}\right)}$	α_{rp}, $\gamma_{rp}$and q_{rp}
Khan	$q_e = \frac{q_{mk} \alpha_k C_e}{\left(1 + \alpha_k C_e\right)^{\gamma_k}}$	α_k, $\gamma_k$and q_{mk}
Fritz and Schhunder	$q_e = \frac{q_{mfs} a_{fs} C_e^{g_{fst}}}{\left(1 + a_{fs} C_e^{g_{fst}}\right)}$	α_{fs}, $\gamma_{fst}$and q_{mfs}
Linear	$q_e = K_p C_e$	k_p
Loading ratio	$q_e = \frac{q_{ml} \left(b_{L1} C_e\right)^{(1/k_l)}}{1 + \left(b_{L1} C_e\right)^{(1/k_l)}}$	$q_{mL,}$ $b_{Ll}$and k_l
Four parameters	$C_e = \alpha_1 Q_e^{\left(\alpha_2 q_m + \alpha_3\right)}$	$\alpha_{1,}$ $\alpha_{2,}$ α_3 and q_m
Dubinin–Radushkevich	$q_e = X_m Exp\left(-k\varepsilon^2\right)$	X_m, k and ε
Statistical	$q_e = \left(\frac{kC_e + (kC_e)^2 \Gamma_{ii}}{1 + kC_e + (kC_e)^2 \frac{\Gamma_{ii}}{2}} \right)$	k
Halsey	$q_e = \left(\frac{k_H}{C_e}\right)^{\frac{1}{n_H}}$	$k_H$and n_H
Koble - Corrigan	$q_e = \frac{a_k C_e^{g_k}}{\left(1 + b_k C_e^{g_k}\right)}$	$\alpha_{kc,}$ β_{kc} and γ_{kc}

Table 3. Equilibrium models and the values of their constants

Source of wastewater	Langmuir model			Freundlich model				Temkin model			Activated sludge model				Redlich - Peterson model			
	a_L(L/mg)	b_L(mg/g)	R^2	k_f(mg/mg)	[1/N_f[(mg/L)	N_f(L/mg)	R^2	a_t (L/mg)	b_t(mg/g)	R^2	k_m(mg/g)	[1/N_m] (mg/L)	N_m(L/mg)	R^2	α(L/mg)	β(mg/g)	γ(mg/g)	R^2
Synthetic	0.276	6.039	0.964	1.486	2.543	0.393	0.999	3.685	18.853	0.967	4292.3	1.111	0.900	0.969	1.451	0.140	0.634	0.822
Raw water	0.725	5.461	0.998	5.051	1.069	0.936	0.999	1.754	0.574	0.997	22.287	0.455	2.198	0.993	4.184	1.247	0.086	0.818
Domestic Institution	0.076	22.779	0.991	0.914	0.519	1.926	0.956	1.096	0.937	0.894	0.253	0.697	1.435	0.937	17.057	15.157	0.353	0.840

Source of wastewater	Hasley model			Koble –Corrigan model				Fritz- Schhundler model				Sips model				Langmuir- Freundlich model			
	N_h(L/mg)	K_h(mg/mg)	R^2	α_{kkc} (L/mg)	β_{kc}(mg/g)	γ_{kc} (mg/g)	R^2	α_{sc} (L/mg)	q_{sc}(mg/g)	γ_{sc} (mg/g)	R^2	α_{tts} (L/mg)	β_{ts}(mg/g)	γ_{ts} (mg/g)	R^2	q_m(mg/g)	K_t(L/mg)	K_{lf}(mg/g)	R^2
Synthetic	0.125	15.55	0.845	1.445	0.036	2.576	0.988	2.045	0.728	2.542	0.999	1.445	0.036	2.576	0.988	2.045	0.728	2.542	0.999
Raw water	14.577	62.80	0.999	4.810	0.108	0.967	0.962	2.410	2.165	1.086	0.999	4.810	0.108	0.967	0.962	2.410	2.165	1.086	0.999
Domestic Institution	0.552	13.362	0.795	2.974	0.045	1.376	0.956	1.776	0.734	0.716	0.942	2.974	0.045	1.376	0.956	1.776	0.734	0.716	0.942

isotherm. The linear form is given in equation (22a) from which the constants q_m, K_{LF} and K_t which characterized the isotherm can be determined.

$$\frac{1}{q_e} = \left(\frac{1}{q_m K_t}\right)\left(\frac{1}{C_e^{K_E}}\right) + \frac{1}{q_m} \tag{22a}$$

Plotting ratio of inverse of equilibrium concentration and equilibrium parameter on the left hand side against equilibrium concentrations the unknown parameters were found (Figure 23). From the figure the values of q_m, K_{LF} and K_t were obtained. The estimated adsorption parameters for the Langmuir- Freundlichmodel are shown in Figure 23 and Table 3. The values of q_m (0.728 mg/g); K_{LF} (2.542 mg/g) and K_t (2.045 L/mg) by the Langmuir- Freundlich isotherm for synthetic wastewaters, q_m (2.165 mg/g); K_{LF} (1.086 mg/g) and K_t (2.410 L/mg) for raw water and q_m (0.734 mg/g); K_{LF} (0.716 mg/g) and K_t (1.776 L/mg) for domestic institutional wastewater suggest that the adsorption capacity of PCR was high and that any large change in the equilibrium concentration of Pb^{2+} ions would not result in a remarked change in the amount of Pb^{2+} ions adsorbed by PCR. The squared correlation coefficients (R^2) for Langmuir- Freundlich isotherm are 0.999, 0.999 and 0.945 for synthetic wastewater, raw water and domestic institutional wastewater respectively. These values of R^2 represent good fitness ($R^2 > 0.95$) of the observed data for adsorption Pb^{2+} ions adsorption onto PCR. The value of q_m, K_{LF} and $K_t$for this model are different from the values documented in literature such as Mamdouth et al [2004], Oke et al [2008] and in Kobya [2004], which indicate that adsorption onto carbon is different from adsorption onto PCC and PES.

Comparison with previous studies on Pb^{2+} adsorption on to other adsorbents: Ho (2007)

Ho(2007) reported that over 9000 articles either as journal articles, conference proceedings or as a book contributions have presented data on adsorption of pollutants from aqueous solutions. Adie et al (2010) is one the such articles, which provides information on adsorption. Adie et al (2010) provides information (summary) on adsorption of Pb^{2+} onto various adsorbents. For some of these adsorbents Langmuir constant were determined for comparison purpose. Table 4 presents summary of the Langmuir constant for Pb^{2+} adsorption onto selected materials as provided in literature, From the table the values of the constant varies from 0.368 mg/g (fly ash) to 1380 mg/g (waste slurry as an adsorbent). This result indicates that PCR is a better adsorbent than wollastonite, china clay and fly ash.

Table 3 shows results of the adsorption capacity analysis of Pb^{2+} onto PCR using equilibrium models. From the table it can be seen these equilibrium isotherm models can be classified into two groups based on the value of their correlation coefficients (R^2).

The classifications are as follows:

Isotherm with correlation coefficients (R^2) less than 0.960: These are Hasley and Redlich–Peterson models. Lower correlation coefficients than 0.960 by these equilibrium isotherm models indicate that they cannot be used to predict adsorption of Pb^{2+} onto PCR accurately.

Isotherm with correlation coefficients (R^2) greater than 0.960: These are Freundlich, Sips, Langmuir- Freundlich, Crombie-Quilty and McLoughin,Temkin,Koble- Corrigan Fritz and Schlunder models. Higher correlation coefficients than 0.960 by these equilibrium isotherm models indicate that they can be used to predict adsorption of Pb^{2+} onto PCR accurately. It also means that there is a good relationship between the data (Oke et al., 2011). This observation is similar to adsorption of Pb^{2+} onto some adsorbents documented in literature and agrees with statements in literature (Oke*et al.,* 2011).

CONCLUSION

It can be concluded based on the study that:

PCR can be used to remove Pb^{2+} from aqueous solution, typical raw water and wastewaters;

Adsorption equilibrium isotherms of Pb^{2+} onto *PCR* can be grouped into two based on correlation coefficients;

Adsorption equilibrium isotherms fit well into Freundlich, Sips, Langmuir- Freundlich, Crombie-Quilty and McLoughin,Temkin,Koble- Corrigan, Fritz and Schlunder models.

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Table 4: Langmuir constants for Pb^{2+} adsorption onto selected materials (Source: Adie et al., 2009)

Material	**R_L (mg/g)**
Waste slurry	1380
Amberlite IR -120	1039
Focus vesiculosus	600
Ascophyllumnodosum	478
Sargassumfluitans	378
Absidiaorchidis	351
Oxidized anthracite	259
Ascophyllumnodosum	257
Algae	251
Spruce sawdust (phosphorylated)	224
Rhizopusnigricans	166
Peat	150
Zoogloearamigra	110
Resting cells	110
Blast furnace sludge	79.9
Inactivated cells	79.5
Tea leaves	78.7
Montmorillonite clay	71.8
Penicilliumchrysogenum	63
Sphagnum peat moss	61.9
Rhizopusarrhizus	55
High carbon content sludge	55
Groundnut husks	39.4
Sphagnum moss peat	30.7
Coke	19.1
Spruce sawdust	15
Illite clay	14.1
Soil	12.6
Linden	12
Kaolinite clay	9.37
Kaolinite clay	6.46
Kaolinite clay	3.93
Wollastonite	1.68
China clay	0.411
Fly ash	0.368
Peat	122
Tea leaves	78.7
Sago	46.6
Groundnut husks	39.4
Grain	35.5
Sphagnum moss peat	30.7
Tree fern	40
HB leaf powder	46.73
HeveaBrasiliensis leaf powder	46.73
Sago waste	46.64
Phosphatic clay	37.20
Live biomass	35.69
NaOH treated spent grain	35.50
Morroccanstevensite	34.16
Sawdust pinussylvetris	22.22
Activated carbon (coconut shell)	26.51
Activated carbon (apricot stone)	22.85
Granular activated carbon	21.50
Carbon nanotubes	16.14
Powdered corn cobs	49.9
Powdered carbon rod (synthetic wastewater, this study)	14.0
Powdered carbon rod (raw water)	26.8
Powdered carbon rod (domestic institutional wastewater)	49.0

SYMBOLS

M : the mass of the adsorbent added (g),

R_R : the percentage pollutant adsorbed (%);

V : the volume of the sample used (300ml) = 0.3L;

q_e : the equilibrium solid-phase concentration of sorbate (mg/mg);

C_0 : the initial concentration of arsenic in the solution (mg/l);

C_e : the experimental concentration in the solution at equilibrium (mg/l)

C_t : the experimental concentration in the solution at time t (mg/l).

γ : theRedlich–Peterson isotherm exponent(mg/g);

α_{fs}, $\gamma_{fst}$and q_{mfs} : Fritz and Schhunder's isotherm parameter (L/mg; mg/g; mg/g respectively);

α_k, $\gamma_k$and q_{mk} : Khan's isotherm parameter (L/mg; mg/g; mg/g respectively);

$\alpha_{kc,}$ β_{kc} and γ_{kc} : Koble-Corrigan's isotherm parameters;

α_{rp}, $\gamma_{rp}$and q_{rp} : Radke-Prausnitz's isotherm parameter (L/mg; mg/g; mg/g respectively);

γ_{rp}, α_{rp},and β_{rp}, : the Radke-Prausnitz's isotherm exponent (mg/g) and parameters (L/mg and mg/g) respectively;

α_t and β_t : Temkin adsorption constants (L/mg) and isotherm parameter (mg/g)respectively;

$\alpha_{t'}$ and $\beta_{t'}$: Redlich–Peterson isotherm parameters (L/mg and mg/g);

$\alpha_{ts,}$ β_{ts} and γ_{ts} : Sips isotherm parameters (L/mg);

$a_L$and b_L : Langmuir adsorption constant (L/mg) and Langmuir isotherm parameter (mg/g) respectively;

K_f and N_f : Freundlich isotherm exponent (g/mg) and Freundlich isotherm parameter (L/mg) respectively;

$k_H$and n_H : Hasley's isotherm parameters;

K_m and N_m : constants for activated sludge model t(l/g) and exponential constant for activated sludge model (mg/g) respectively;

k_p : the isotherm constant for linear model;

q_m, $\alpha_{tt,}$ and γ_{tt} : Toth isotherm parameters (mg/g; L/mg; mg/g respectively);

q_m, K_{LF} and K_t : Langmuir – Freundlich isotherm constants;

$q_{mL,}$ $b_{Ll}$and k_l : Loading ratio's isotherm parameters (L/mg; mg/g; mg/g respectively);

X_m, k and ε : Dubinin-Radushkevich's isotherm parameters;

$\alpha_{1,}$ $\alpha_{2,}$ α_3 and q_m : Four parameters' isotherm parameter (L/mg; mg/g; mg/g respectively)

A : concentration of the metals (mg/L)

AS and WS : acid and water solubility (%)

M_c and Ash : moisture and ash contents (%)

W_1 and W_2 : initial and final weight of PCR after oven dry at 105°C

W_3 : final weight of PCR after 2 hours burnt in the furnace at 550°C

W_4 and W_5 : dry weight of PCR after soaked in water and acid respectively (mg)

VS : volatile solids (mg/g)

M_{cc} : metal concentration (mg/g)

R_L : Langmuir constant

B : metal concentration of obtained from AAS (mg/L)

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